

S100 29 and 30

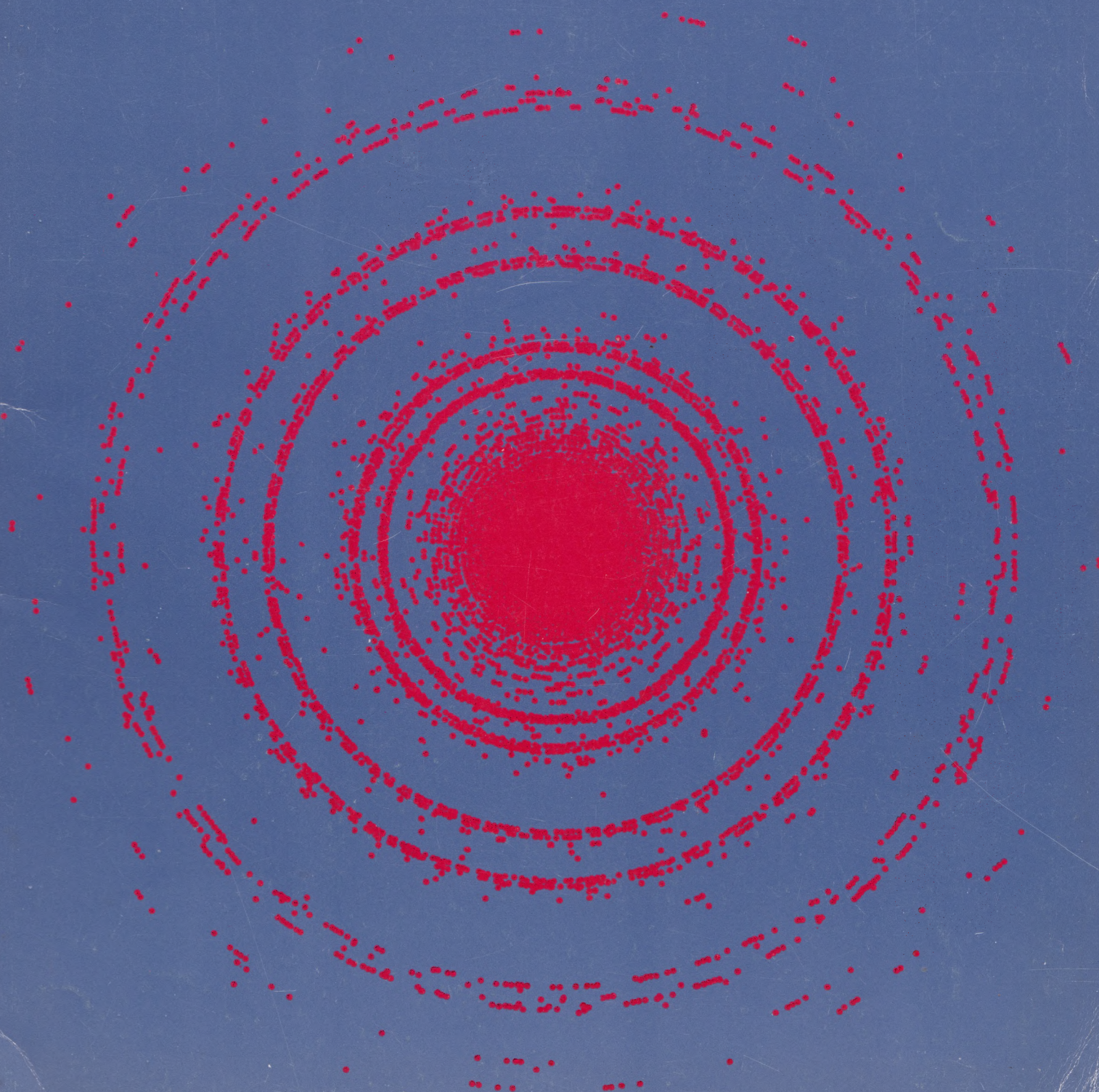
THE OPEN UNIVERSITY



Science Foundation Course Units 29 and 30

Quantum Theory

Quantum Physics and the Atom





The Open University

Science Foundation Course Unit 30

QUANTUM PHYSICS AND THE ATOM

Prepared by the Science Foundation Course Team

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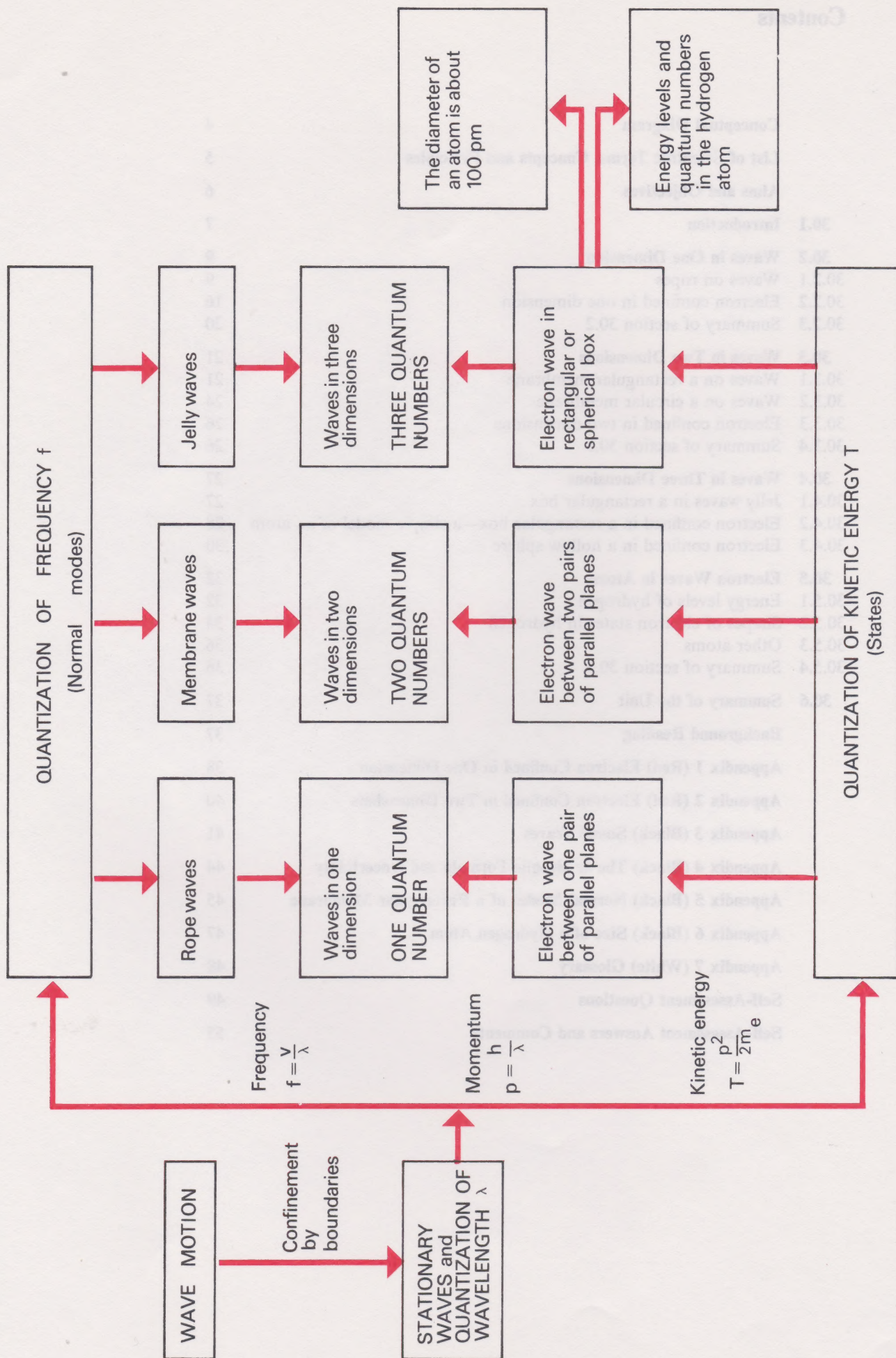


Table A

List of Scientific Terms, Concepts and Principles used in Unit 30

Taken as pre-requisites			Introduced in this Unit			
1	2		3		4	
Assumed from general knowledge	Introduced in a previous Unit	Unit No.	Developed in this Unit	Page No.	Developed in a later Unit	Unit No.
dimension diameter radius	electron reflection of waves transverse wave longitudinal wave wavelength frequency quantum numbers uncertainty relations amplitude of waves probability waves kinetic energy momentum de Broglie formula energy energy level atom ionization energy potential energy electric charge nucleus ion electromagnetic waves photon atomic spectrum periodic table	6 22 22 22 2 2 6, 7 29 2 29 4 3 29 4 6 6 4 2 6 5 2 6 6 7, 8	longitudinal wave transverse wave antinode node quantum number standing or stationary wave normal mode fundamental frequency harmonic overtone resonance boundary conditions wave function zero-point energy degeneracy	9 9 10 10 10 10 12 13 13 13 16 17 19 23		

Scientific terms used in this Unit but not listed above are marked thus † and defined in the glossary (p. 48).

Aims

- 1 To show that when a wave is confined within a limited region of space, the wavelength and frequency can only have certain discrete† and well-defined values which are specified by one or more whole numbers called quantum numbers.
- 2 To extend the electron wave theory introduced in Unit 29 by linking it with the behaviour of confined waves in general, and so develop an understanding of how an electron behaves when confined in an atom.

Objectives

When you have finished this Unit you should be able to:

- 1 Define correctly or recognize the best definition of all the terms, concepts and principles in column 3 of Table A.
- 2 Explain in not more than two hundred words, with suitable diagrams, why a stretched rope will vibrate easily only at certain frequencies and how these frequencies are determined; or select from a list of statements relevant to such an explanation.
- 3 Carry out simple calculations relating velocity, frequency, wavelength and the separation of nodes for one-dimensional waves; identify each normal mode by its overtone number and harmonic, and draw diagrams to illustrate (as in Fig. 4).
- 4 List advantages and limitations of a described experiment (not necessarily familiar) for measuring the velocity of one-dimensional waves; estimate the error in the result.
- 5 Recognize true and false reasons and statements concerning an electron confined, with constant kinetic energy, between two parallel planes; interpret a given expression (equation 7) for its kinetic energy and draw an energy level diagram.
- 6 Predict the general form of the wave-function ψ and also ψ^2 for an electron confined between two parallel planes and having a given variation of potential energy between them.
- 7 Identify the assumptions made in a given model of a hydrogen-like atom and the derivation of its radius (section 30.4.2); assess the validity and relative importance of the assumptions and interpret a given expression for its radius (equation 17).
- 8 Discuss, or recognize reasons for statements concerning, and draw diagrams to illustrate, the wave-function, probability distributions and energy levels of a hydrogen atom.
- 9 Explain, or recognize statements concerning the reason for, the number of quantum numbers needed in any of the examples discussed in the Unit.
- 10 Discuss, or recognize reasons for, statements concerning the concept of 'degeneracy' applied as widely as possible in and beyond the area of this Unit.

Section 1

30.1 Introduction

In Unit 29 you saw that, in order to describe how radiation is propagated, it is necessary to use the mathematics of waves. There we were considering one particular type of wave propagation—from a source to an absorbing screen. But what if the screen were not absorbing? Suppose the radiation were to be reflected. Moreover, suppose the radiation were to be trapped on all sides by reflecting walls so that it went continually back and forth—what then? Would such an arrangement give rise to any new features? You have only to listen to a musical instrument for the answer. Pluck a violin string or blow a flute—what do you hear? You hear a particular combination of notes, a musical sound and not just a mere noise. This is because these instruments rely on the repeated reflection of waves back and forth, and only certain waves can be confined in this motion. If there are restrictions on the musical notes that can be sounded together on a flute might there not be similar restrictions when electron radiation is confined between reflecting planes? The answer must be *yes*, for the mathematics is just the same. However, this is no mere academic question; all electrons bound in atoms have probability waves that are confined to a small region of space. This, then, is the subject of this Unit—the study of waves, especially electron probability waves, which are confined to a limited region of space and the consequences of such confinement.

At last we shall be able to give you some understanding of the mysterious quantum numbers introduced in Unit 7. The reasons for the existence of these quantum numbers will become clear in sections 30.2 to 30.4. The terminology used in a description of the hydrogen atom is first introduced on p. 29, but even for this simple atom the full mathematics is too advanced for an introductory course. The important concepts will therefore be developed largely by analogy with simpler experiments in one, two and three dimensions in which a wave is confined to a limited region of space. The consequences of such restrictions will be stressed and, at each stage, applied to an electron in a similar situation. This will lead quite naturally to a wave model of the hydrogen atom. Other atoms will also be considered briefly.

At the end of this Unit you should understand basically why atoms are just the size that they are (section 30.4.2), why the electrons in them can only have certain well-defined values of energy called energy levels (sections 30.2.2, 30.3.3, 30.4.2 and 30.5.1), and what can be said about the position of the electron in the atom (section 30.5.2). As a bonus you will also have learned a lot about the general theory of waves in confined regions, a subject which has applications in many branches of science, not least in a better understanding of what goes on inside a musical instrument (see pp. 13 and 25).

There is inevitably a certain amount of mathematics, but do not be alarmed about this. As much mathematics as possible has been relegated to black-page appendices and you should not find the remainder too difficult. In particular, we do not expect you to learn by heart all the equations and derivations given in this Unit, but you should of course be able to answer questions on all of them. However, certain equations

are so important and so frequently used that you will find it a great advantage to learn them; these are:

- equation 1 on p. 12;
- equation 4 on p. 18;
- equation 5 on p. 18.

You may like to mark these equations now to remind yourself of their importance when you come to them. Similarly the derivation of equation 3 on p. 12 and that of equation 7 on p. 18 are so typical of the logic of this Unit that you should study them very carefully and make sure that you understand them before reading on.

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At last we shall be able to give you some understanding of the experiment of quantum numbers introduced in Unit 1. The reason for the existence of these quantum numbers will become clear in sections 30.1 to 30.4. The terminology used in a description of the hydrogen atom is first introduced on p. 32, but even for this single atom the full mathematics is too extensive for an introductory course. The important concepts will therefore be developed largely by analogy with simpler experiments in one, two, and three dimensions in which a wave is confined to a limited region of space. The consequences of such restriction will be stressed and, as each stage, applied to an electron in a similar situation. This will lead quite extensively to a wave model of the hydrogen atom. Other atoms will also be considered briefly.

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30.2 Waves in One Dimension

In this section we want you to understand what happens when electron radiation is confined in only one dimension. Then, in later sections, you will find that the effect of confining it further is not qualitatively very different. However, before studying electrons at all, it is easier to introduce the basic ideas with waves that you can actually see, such as waves on a rope or wire.

30.2.1 Waves on ropes

Consider a rope clamped firmly at one end and held under tension at the other.

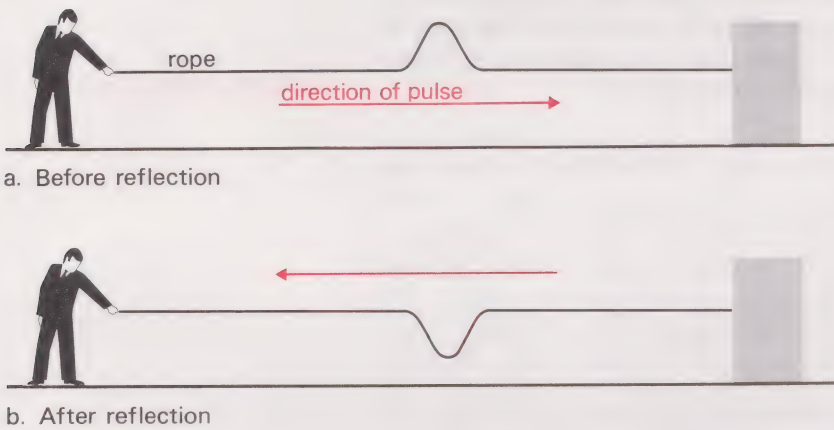


Figure 1 Pulse on a rope.

If a pulse† is sent along the rope (Fig. 1(a)) it is reflected from the fixed end and returns upside down (Fig. 1(b)). You can easily try this yourself sometime, but a reasonable length of rope (at least 5 metres) is needed to see the pulse clearly because it travels quite fast. The rope should also be quite flexible.

Note that, although the rope pulse in Figure 1 occupies two dimensions in space, the pulse is propagated only in a single dimension, i.e. along the rope. It is important to distinguish clearly between the motion of the rope and the motion of the pulse or wave. We shall use the term ‘one-dimensional wave’ throughout the Unit to mean that the *wave* travels only along a single line regardless of how the *rope* itself moves. A ‘two-dimensional wave’ will mean a *wave* which travels in any direction on a (two-dimensional) flat surface, regardless of any motion of the *medium* in which the wave exists. The vertical direction used for the displacement of the rope means that the displacement is at right angles to the direction of the wave—this is an example of a *transverse wave* (or S wave in the notation of Unit 22, section 22.4). Sound waves on the other hand are *longitudinal waves* (P waves) because the displacement of the medium is in the same direction as that of the wave—see Appendix 3 (Black). In other kinds of one-dimensional wave, such as a temperature pulse travelling along a metal bar when one end is suddenly heated and then cooled again, no other spatial dimension is needed.

transverse wave

longitudinal wave

The same experiment can be done with a wave consisting of a short train† of pulses (Fig. 2) though it is harder than with just a single pulse.

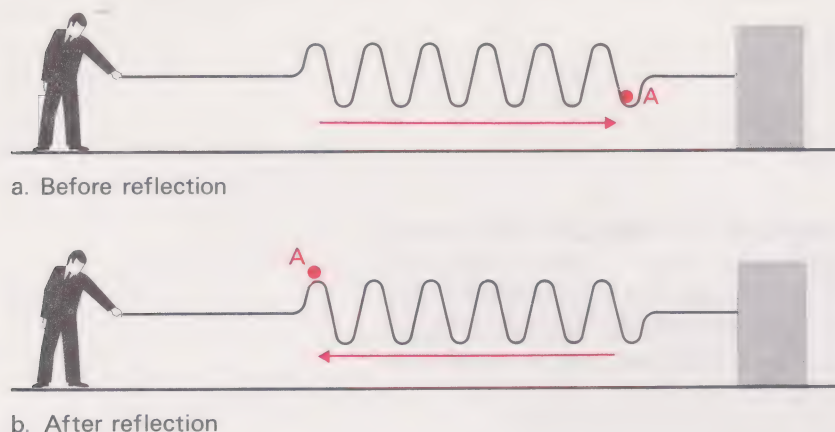


Figure 2 Wave on a rope.

The wave train is again inverted top-to-bottom. If you cannot see this, look at the peak A and remember that the leading pulse is reflected first so that left-to-right inversion also takes place. What interests us is the time during the process of reflection when part of the wave is still going to the right, part is going to the left and the two parts are crossing each other. To see this more clearly, it is simpler to consider two separate but identical wave trains travelling in opposite directions along an infinite rope. The actual displacement of any bit of the rope is then the sum of the displacements due to the two waves taken separately—this is called the *principle of superposition* (Unit 22, section 22.4.10).

principle of superposition

Figures 3(a) to 3(e) show a series of close-up ‘snapshots’ of part of the two separate wave trains (in black) and the combined wave train (in red) at successive equal intervals of time. In each diagram the upper wave is moving to the right and the lower one to the left. Follow each of the two waves through the five diagrams to convince yourself of this. The time interval τ between successive diagrams is, for convenience, equal to the time taken for each wave train to travel a quarter of a wavelength. The first snapshot is at the instant when the two wave trains exactly coincide.

The points labelled A to E are spaced $\frac{1}{4}\lambda$ apart. Figure 3(e) is the same as Figure 3(a), and the cycle repeats indefinitely. You will notice that the waves momentarily reinforce each other and then cancel out. Look more closely and you will see two extreme kinds of point—at A, C and E the two waves *always* cancel and the rope is never displaced there at all, whereas B and D both vibrate strongly though in opposite directions. Points like A, C and E, at which there is no vibration, are called *nodes*; points of maximum vibration like B and D are called *antinodes*.

node
antinode

Figure 3(f) is a ‘time-exposure’ of the combined wave trains; you can imagine this as the result of superimposing all the ‘instantaneous photographs’ above it, and many more intermediate ones. This is called a *stationary wave* or *standing wave* because it does not appear to travel either to the left or to the right.

standing wave

What is the least separation between:

- (a) two nodes?
- (b) two antinodes?
- (c) a node and an antinode?

Now think back to the original situation in Figure 2. The wave train moving from right to left is the wave train reflected from the clamp at the right-hand end. During the time that the wave train is being reflected

- (a) Consecutive nodes such as A and C are spaced $\frac{1}{2}\lambda$ apart.
- (b) $\frac{1}{2}\lambda$ —exactly the same distance as two nodes.
- (c) $\frac{1}{4}\lambda$

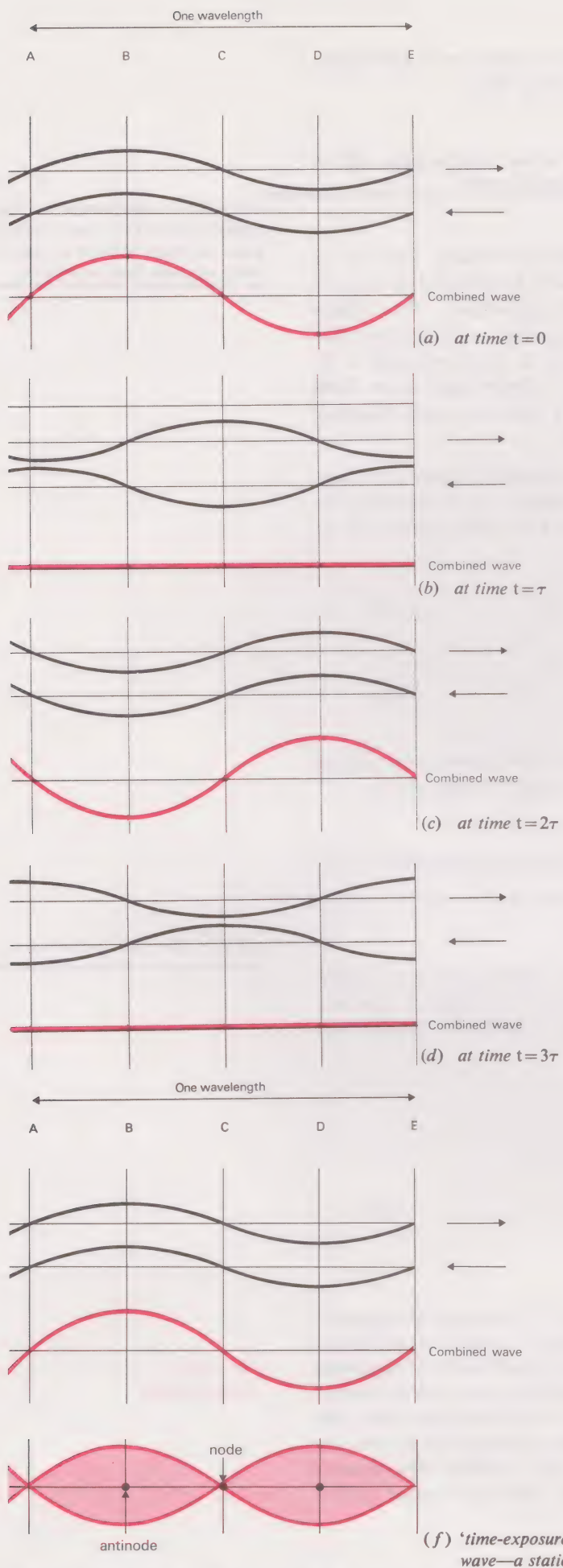


Figure 3 Superposition of wave trains in opposite directions and resulting stationary wave.

and the two wave trains are crossing each other, the clamp must correspond to some point on the stationary wave pattern (Fig. 3(f)).

Which kind of point on the stationary wave do you think the clamp will be? Will it be a node, an antinode or some intermediate point?

It must be a node, because the rope cannot vibrate at the clamp, and a node is the only kind of point in Figure 3(f) where the rope does not vibrate.

Suppose that point E on Figure 3 corresponds to the clamp. There is, of course, no reason why the rope should not also be clamped at A or C as well as E; these two points are not vibrating anyway, so a clamp cannot make any difference. Suppose A (or any other node further to the left) is suddenly clamped while the wave train is being reflected at E. Then the wave train is trapped between two clamps and, apart from losses, the vibration will continue indefinitely with the wave bouncing back and forth between the two clamped ends.

It follows that since the distance between consecutive nodes is $\frac{1}{2}\lambda$ and both ends of the rope are nodes, then the length c of the rope must be an exact number of half-wavelengths, two in fact if the clamps are at A and E. In the general case,

$$c = n(\frac{1}{2}\lambda) \dots\dots\dots(1)$$

where $n = 1, 2, 3, 4$, etc.

$$\therefore \lambda = \frac{2c}{n} \dots\dots\dots(2)$$

The frequency of oscillation of a rope is equal to the number of complete to-and-fro oscillations it makes per unit time (Unit 2, section 2.2.1).

How is the frequency f of the oscillation related to the wavelength λ and the wave velocity v ?

$$v = \lambda f$$

$$\text{or } f = \frac{v}{\lambda} \text{ (See Unit 2, equation 1)}$$

The velocity v of the waves can easily be shown experimentally to depend only on the tension in the rope and the mass per unit length. v does not depend at all on the frequency f , as you will see in the TV programme. The frequency is therefore given by

$$f = \frac{v}{\lambda} = \frac{v}{(\frac{2c}{n})}$$

$$f = n(\frac{v}{2c}) \dots\dots\dots(3)$$

(where $n = 1, 2, 3, 4$, etc.)

The rope can only oscillate with certain discrete† frequencies corresponding to whole-number values of n , so that an exact number of half-wavelengths fits into the length c . This is an example of *quantization* of frequency and n is called a *quantum number*. When something is *quantized*, this means that it can have only certain precise values, rather than any value. *The existence of such discrete frequencies is a direct consequence of the confinement of the wave within a limited region.* The possible rope patterns and corresponding frequencies are collectively called the *normal modes**

quantization
quantum number

normal mode

* Do not confuse these modes with nodes (p. 10).

of the rope. This is a general term covering all stationary-wave patterns in any number of dimensions. Now look at the conceptual diagram on p. 4; the left part and the upper part summarize the ideas developed so far.

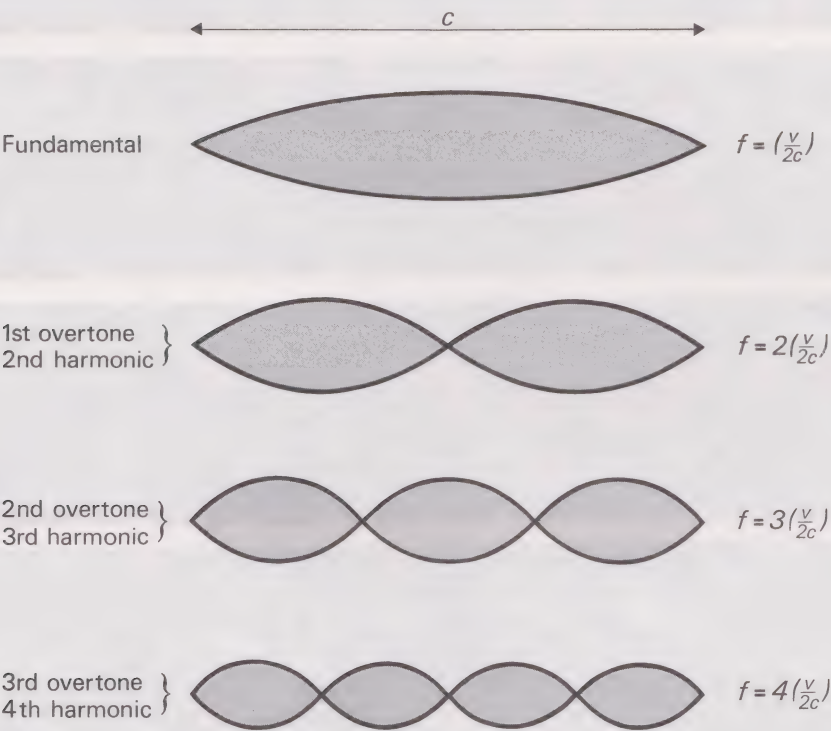


Figure 4 Normal modes of a rope or wire.

The normal modes for a vibrating rope (or wire) and the frequencies of oscillation for values of *n* up to 4 are shown in Figure 4. You will see these demonstrated in the TV programme. Note the names of the normal modes on the left-hand side of this figure.

The *overtone*s are numbered in order. The *harmonic* number is defined as the multiple of the *fundamental* frequency. Thus the 3rd overtone clearly has a frequency 4 times the fundamental—it is therefore called the 4th harmonic. The term ‘first harmonic’ is not used; it would be a synonym for ‘fundamental’.

overtone

What harmonic will the 5th overtone be?

The 6th harmonic.

Suppose a stretched rope is arranged so that a vibration from some other source can be transmitted to it through, for example, its end supports. Then, when this external vibration has a frequency which is equal or nearly equal to that of one of the normal modes of the rope, a strong vibration of the rope in that mode will build up. When the frequency does not correspond to any normal mode the response of the rope is very small. It is like pushing someone on a swing; you have got to push at the right moments or the swing will not get going properly. The large response of the rope when driven at a normal mode frequency is an example of *resonance*. Figure 5 shows a series of photographs of a vibrating string in resonance with a vibration which is transmitted to the string through its right-hand end. Notice that this end is almost a node in spite of the vibrator to which it is attached. You will also see this demonstrated in the TV programme.

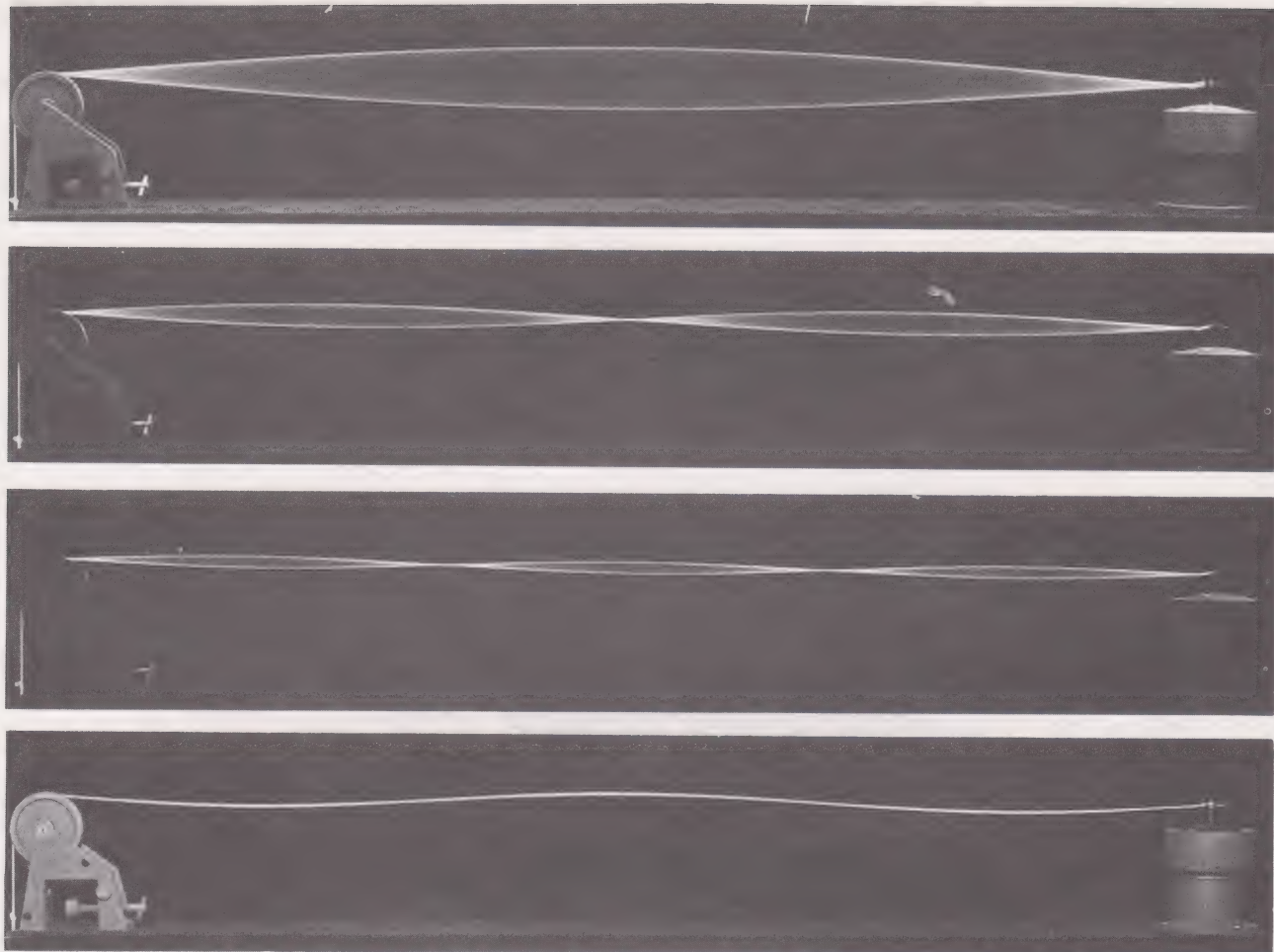


Figure 5 Photographs of a vibrating string. The first three pictures are time-exposures over many complete vibrations; the lowest picture is an ‘instantaneous’ snapshot of the $n=3$ normal mode.

In a free vibration, without any external effect transmitted to it, the actual motion of the rope may be one of the normal modes or more usually some combination of them all with various amplitudes. For example, a guitar string plucked at its centre (Fig. 6) can be shown to vibrate with an

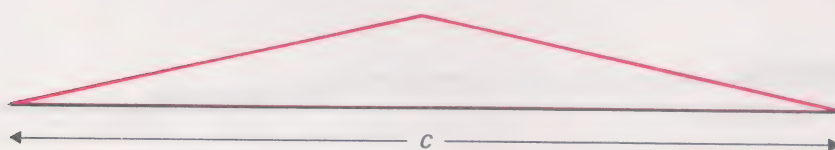


Figure 6 Guitar string at the moment of release.

infinite number of normal modes having the following relative amplitudes:

Fundamental	3rd Harmonic	5th Harmonic	7th Harmonic ...	n th Harmonic (n odd) ...
+ 1	$-\frac{1}{9}$	$+\frac{1}{25}$	$-\frac{1}{49}$...	$\pm \frac{1}{n^2}$...

No even harmonics are present in this vibration and if you look again at Figure 4 you should see that this is not surprising.

Why does Figure 4 suggest that a guitar string plucked at its centre will not have even harmonics in its vibration?

The analysis of a wave shape, such as the guitar string of Figure 6, into the various harmonics of which it is composed is called *Fourier Analysis*. You have met it before in Unit 29, section 29.1.5. The string will not return to its original position until the end of one complete cycle of the fundamental frequency. Before this time, it will go through a complex series of shapes due to the presence of the higher frequencies. The tone of the note is determined by the relative strengths of the various harmonics and hence by the position in which the string is plucked (or bowed in the case of a violin). In musical instruments such as the guitar, violin, viola, cello and double-bass, the tone will also depend on the sound-box on which the string is mounted, since this determines to a large extent the relative amplitudes of the harmonics actually emitted as sound-waves. It is the sound-box which makes a Stradivarius violin command such a high price—plus the scarcity, of course.

Because the even harmonics all have zero amplitude (a node) at the centre whereas the guitar string has a maximum there. This does not prove that no even harmonics can be present, but it does make their absence at least very plausible.

Fourier analysis

YOU SHOULD NOW TRY HOME EXPERIMENT 1. This is an optional experiment which requires access to a piano. Do not worry if you are unable to attempt it.

Sound waves in a tube closed at both ends obey exactly the same equations as waves on ropes, but the wave is a pressure wave in the air filling the tube. In musical wind instruments like the trumpet, clarinet and organ, the pitch of the note is determined by the effective length of a tube in which a stationary sound wave is set up. However, in most cases the tube is open at one end; this makes a difference to the theory, though not to the basic principles involved. The tone of the note (e.g. the difference between a trumpet and a clarinet playing the same note) depends, as with a stringed instrument, on the relative strengths of the many normal modes which can exist.

YOU SHOULD NOW TRY HOME EXPERIMENT 2. You can easily complete this experiment without knowing the theory, and it is probably more fun to do it this way. The theory is given in Appendix 3 (Black) for reference *after* the experiment.

It is not a general property of resonant systems that the normal mode frequencies are harmonics (exact multiples) of a fundamental frequency. In some cases (as in section 30.3) they are related by straightforward equations, but are not harmonics of the fundamental frequency. In others the relationship is only through complicated mathematical functions.† *Nevertheless, in all cases there is a mathematical expression for the frequencies of the normal modes, including one or more quantum numbers taking only integral† values.*

Already more than half of the scientific terms and concepts listed in column 3 of Table A have been introduced. Many of these will form the basic vocabulary of the rest of the Unit. Before reading on, turn back to Table A and check (from the page numbers given) which terms and concepts you should already understand. Think carefully about each of them; if you are unsure about the meaning of any, go over the relevant pages again now. Then, for revision, copy out equations 1 to 3 on a separate sheet of paper and open the Unit at Table A. Try to work through the ideas contained in this section, either in your mind or on paper, until you are quite sure that you understand what each symbol represents in the equations and how they fit into the story.

Now turn to the first four of the Self-Assessment Questions (p. 49). You may attempt all four of these questions if you like; alternatively you may prefer to select just one or two which you consider will help you the most.

30.2.2 Electron confined in one dimension

In the previous section, you have seen how a rope wave which is confined to move between two clamps forms a stationary wave. Whereas the wave on a rope clamped only at one end can have any wavelength and frequency, the second clamp causes a severe restriction—only certain discrete wavelengths and frequencies are possible (corresponding to the resonance frequencies mentioned on p. 13) and these are determined by a quantum number. This restriction takes the form of a specified amplitude of the wave at the ends of the rope (i.e. at the two clamps); in this case the specified amplitude is zero, making these points nodes. The existence of a specified amplitude at the ends (whether zero or not) is called a *boundary condition*. The two boundary conditions on the rope are the direct cause of the quantization of vibration frequencies and of the existence of normal modes determined by a single quantum number n .

boundary condition

Electron propagation is also governed by wave mathematics, as you have seen in Unit 29. As a first step to understanding the effects of confining an electron in an atom, it is very helpful to imagine the electron radiation trapped between two infinite planes† which reflect it to and fro between them (Fig. 7).

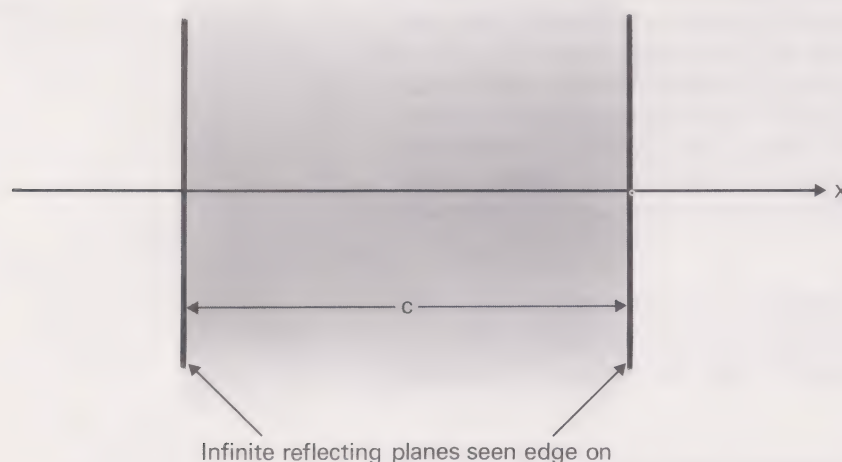


Figure 7 Electron radiation is considered to be confined in one dimension between the two parallel reflecting planes.

Heisenberg's Uncertainty Relations (Unit 29, section 29.4) show that it is not possible to say that the electron is both on the x -axis and moving parallel to it. This would imply a precise knowledge about both its position and momentum in a *transverse* direction, which is impossible. However, we can *trade* knowledge about its transverse position for knowledge about its transverse momentum. By sacrificing *all* knowledge of its perpendicular distance from the x -axis we can stipulate that its transverse momentum is zero—i.e. it is moving parallel to the x -axis. This is, of course, an entirely hypothetical experiment since the reflecting planes would be impossible to set up. Nevertheless, you will find this thought-experiment a very useful stepping-stone towards understanding how an electron behaves in an atom.

The electron radiation cannot escape from between the two planes, so the mathematical wave must have zero amplitude outside this region. Between the two planes the wave is reflected to and fro just like the rope wave between its two clamps and therefore exists as a stationary wave. It is not unreasonable to expect that, like the rope wave, the electron

wave must go smoothly to zero at the two boundaries (the two reflecting planes) in order to avoid a sudden discontinuity† there. This means that there will be a node at each boundary.

So the problem is simply to fit a stationary wave into a limited length c in such a way that there is a node at each end. You already know exactly how to do this from the last section (30.2.1).

How must the wavelength λ of the electron be related to the distance c between the two planes?

c must be an integral multiple of $\frac{1}{2}\lambda$.
 λ can have only certain values which make this true.

As in section 30.2.1

$$\lambda = \frac{2c}{n} \text{ (equation 2)}$$

(where $n = 1, 2, 3$, etc.)

The electron waves between the two reflecting planes can be represented by the graphs of Figure 4 in which the amplitude must now represent the amplitude of the electron wave rather than a physical displacement sideways of the rope. However, it is customary to draw electron waves as ‘snapshots’ of the wave rather than as ‘time-exposures’. The two electron states* of longest wavelength are shown in Figure 8(a).

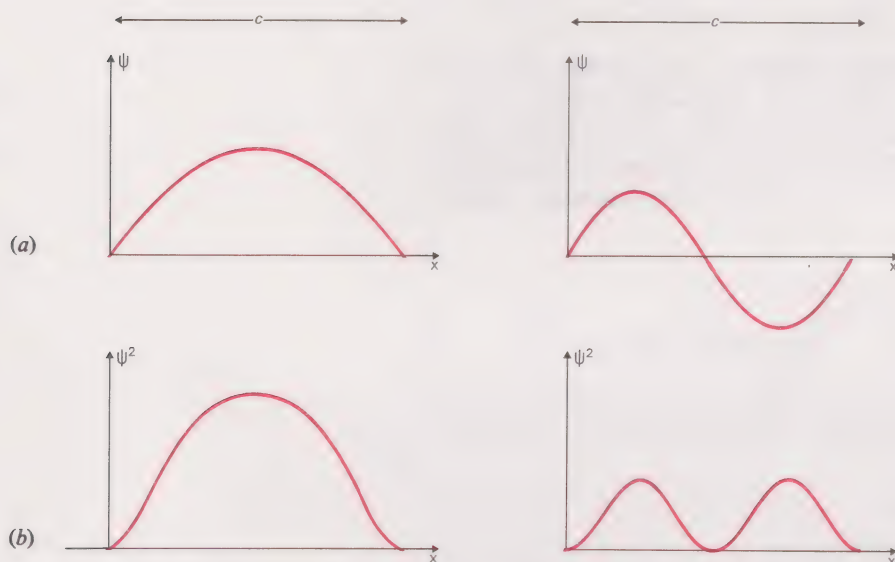


Figure 8 Wave function of an electron confined in one dimension between two parallel planes.

The mathematical functions which represent electron waves such as those in Figure 8(a) are called electron *wave functions*. The Greek symbol ψ (pronounced psi) is used to represent a wave function.

wave function

The modern interpretation of the meaning of the electron wave function was first suggested by Born in 1926. The probability of finding the electron in any small region of fixed volume is proportional to ψ^2 ,** shown in Figure 8(b). This is consistent with the detection of a light wave the intensity of which is determined by the square of its amplitude (Unit 28, section 28.4). The intensity of light on a screen is also proportional to the

* The word ‘state’ is used for an electron as an exact equivalent to ‘normal mode’ for a rope wave.

** It is technically correct to write $|\psi|^2$ rather than ψ^2 . The modulus signs (see MAFS Glossary, p. iv) have a specialized meaning here which is beyond the scope of this Foundation Course. We mention this in case you should be confused by the notation which you will find in most textbooks, but the distinction need not worry you at this stage.

probability of a photon arriving there, so the probability of finding a photon of light is proportional to the square of the amplitude of the light wave. The same is true for electron radiation. Thus for $n=1$, the electron is most likely to be found in the middle of the region and not very likely to be found near the ends. For $n=2$, Figure 8(b) shows that the electron will not be found at all at the ends and at one other place.

Where else will the electron not be found for $n=2$?

The next stage is to relate this electron wave to the kinetic energy of the electron. This is in principle an observable quantity, whereas the wave is never observed directly; only its effects are seen. The kinetic energy can be found from the momentum.

The electron will not be found where ψ^2 is zero—i.e. in the centre of the region, midway between the two reflecting planes. If you do not understand this, read the last paragraph carefully again. The electron is least likely to be found where ψ^2 is very small and most likely to be found where ψ^2 is greatest.

How is the momentum p of the electron related to its wavelength λ ?

The momentum and wavelength of any particle-wave are related by the de Broglie formula:

$$p = \frac{h}{\lambda} \dots\dots\dots(4)$$

(See Unit 29, equation 2)

where h is Planck's constant.

It is not difficult now to get a simple expression for the possible values of kinetic energy that the electron can have. Remember, discrete wavelengths mean discrete momenta (equation 4), and discrete momenta mean discrete values of kinetic energy. Provided that the velocity v of the electron is always much less than the velocity of light,* the electron's kinetic energy T can be expressed as:

$$T = \frac{p^2}{2m_e} \dots\dots\dots(5)$$

(See *MAFS*, section 1.E.6)

where m_e is the mass of an electron; a subscript e has been added to m to avoid confusion in later sections where m is used to stand for a quantum number.

Substituting for p from equation 4,

$$T = \left(\frac{h}{\lambda}\right)^2 \left(\frac{1}{2m_e}\right) \dots\dots\dots(6)$$

and substituting for possible values of λ from equation 2,

$$T = \left(\frac{n}{2c}\right)^2 \cdot \left(\frac{h^2}{2m_e}\right)$$

$$\therefore T = n^2 \cdot \left(\frac{h^2}{8c^2m_e}\right) \dots\dots\dots(7)$$

where $n=1, 2, 3$, etc.

The term in brackets in equation 7 contains three quantities of which two (h and m_e) are physical constants and the third (c) is a fixed length in a particular thought-experiment—see Figure 7. So the term in brackets does not change in value. This means that the kinetic energy T can be written as a constant multiplied by n^2 . Each value of the quantum number n (1, 2, 3, etc.) gives a different value of kinetic energy. These kinetic

* You may well wonder whether this assumption is justified. The kinetic energies of electrons in atoms are such that the velocities are always much less than the velocity of light. However, in very precise calculations a relativistic formula for the kinetic energy is used. Equation 5 is sufficiently accurate for the purposes of this Unit.

energies are examples of energy levels. The quantization of kinetic energy for electrons is analogous to the quantization of frequency for rope waves. Turn back to the conceptual diagram on p. 4 and you will see this relationship. The immediate consequence of boundary conditions is the quantization of wavelength. For waves like those on ropes, the frequency is then calculated, but for electron waves (or any particle waves) the kinetic energy is a more useful quantity to work out.

It is important that you should understand clearly the argument of the last page or two, because a logically similar argument will be used again in later sections and forms the basis of all quantization of energy levels. If you have found real difficulty turn to Appendix 1 (Red).

It is interesting to find the lowest value of kinetic energy that the electron can have. This is obtained by setting $n = 1$ in equation 7. Call it T_1 .

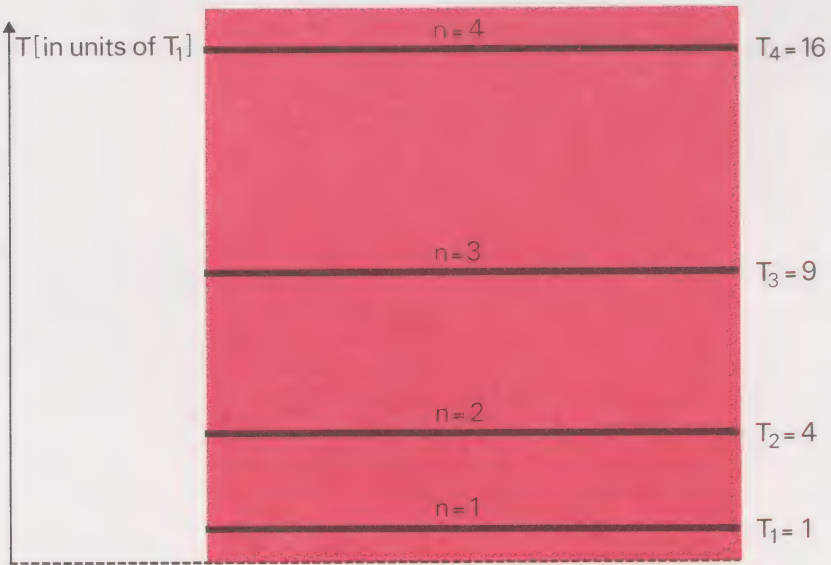
Then
$$T_1 = \frac{h^2}{8c^2m_e} \dots\dots\dots(8)$$

You probably expected the lowest value of kinetic energy to be zero; *it is not*. No kinetic energy lower than that given by equation 8 is possible, for T_1 corresponds to the longest wavelength (and therefore lowest momentum) of a stationary wave that will fit between the two boundary planes. This lowest-energy state of the electron is called its ‘ground-state’ (you met this term in Unit 6, section 6.5.2 in the context of atomic energy levels). The energy of this lowest state is called the *zero-point energy*—you have met this before in Unit 11. You may perhaps be wondering whether you should be distinguishing between (total) energy and kinetic energy. In this thought-experiment the potential energy does not vary anyway, so no distinction need be made.

A zero value for the lowest kinetic energy of an electron confined between two planes would also be contrary to Heisenberg’s Uncertainty Relations.

Why is this so?

Figure 9 shows an energy level diagram for an electron confined between two parallel planes. Kinetic energy T is plotted vertically in units of T_1 , i.e. the ratio T/T_1 is plotted. The possible values of kinetic energy are T_1 , $4T_1$, $9T_1$, $16T_1$, etc.



zero-point energy

Because if the kinetic energy is zero, its value is precisely known. So there is no uncertainty in the kinetic energy or in the x -component of the momentum; $\Delta p = 0$. Further, the electron is somewhere in the region between the two planes, so $\Delta x = c$. Multiplying, $\Delta p \cdot \Delta x = 0 \times c = 0$ which is inconsistent with the Uncertainty Relations (see Unit 29, section 29.4). This point is developed further in Appendix 4 (Black).

Figure 9 Energy levels for an electron confined in one dimension between two parallel planes.

You should now understand all but one of the terms and concepts listed in column 3 of Table A. Study these carefully and refer back if necessary to the relevant pages. Then try to summarize in not more than one page the main ideas developed so far in the Unit. Our summary is given below; it is not intended to include everything, but it does pick out the major themes.

30.2.3 Summary of section 30.2

The confinement of a wave between two boundaries gives rise to a stationary wave having only certain discrete wavelengths determined by a single quantum number n . This applies both to a rope wave and to the mathematical wave used to describe electron propagation. It follows that the *frequency* of a rope wave is also quantized since this is directly related to the wavelength. For an electron wave confined in an analogous manner, the *momentum* is deduced from the de Broglie formula and the *kinetic energy* from the momentum—both of these are therefore quantized too. The possible values of kinetic energy are plotted on an energy-level diagram; they are not equally spaced. The lowest value (zero-point energy) is not zero; this is in accordance with Heisenberg's Uncertainty Relations. The stationary electron wave (called a wave-function) has a physical interpretation; the square of the wave-function at any point is a measure of the probability of finding an electron there. This leads to the rather surprising result that there are certain positions (except in the ground state) between the two planes where the electron will never be found.

Now turn to the Self-Assessment Questions and attempt numbers 5 to 7 (pp. 51-2).

30.3 Waves in Two Dimensions

If you have found very great difficulty in understanding this Unit so far, the following section (30.3) may be skimmed quickly in order to pick out the major ideas; these are also summarized on p. 26.

It is time to extend the theory now from one to two dimensions and to see what difference this makes to the ideas of quantization developed in the last section. Once again we want you to study first a system of waves that you can actually see. Then, when the effects of confining the waves in two dimensions are clear, the results will be carried over to electron waves, just as in the last section (30.2). The justification for doing this will come in section 30.5, when the electron wave theory is applied successfully to a real atom. The simplest two-dimensional example to study consists of a rubber membrane stretched on some kind of frame so that it can vibrate like a drum.

30.3.1 Waves on a rectangular membrane

A *rectangular* membrane is the easiest shape to deal with because this leads to particularly straightforward mathematics. The membrane is stretched under a uniform tension in all directions and is of uniform composition and thickness so that a wave has the same velocity in all directions. This wave velocity v is the same for all frequencies by analogy with waves on ropes—a membrane is after all only a rope with a rather unusual shape of cross-section.†

The possible wavelengths λ of stationary waves on the surface of the membrane are given by:

$$\frac{1}{\lambda^2} = \left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2c}\right)^2 \dots\dots\dots(9)$$

where $m = 1, 2, 3, \text{etc.}$
 $n = 1, 2, 3, \text{etc.}$ } quantum numbers
 b, c are the lengths of the two sides of the membrane.

Equation 9 is derived in Appendix 5 (Black); it is more similar to the one-dimensional case than you might at first realize. In one dimension:

$$\lambda = \frac{2c}{n} \text{ (equation 2)}$$

Squaring and inverting,

$$\frac{1}{\lambda^2} = \left(\frac{n}{2c}\right)^2 \dots\dots\dots(10)$$

The length c may be compared with one dimension of the membrane. Equation 9 for the two-dimensional case is then identical to equation 10 for one dimension with the addition of an extra term for the second dimension. Two quantum numbers m and n are needed to specify a particular normal mode, because the wave can be resolved into two independent waves (one in each dimension of the membrane) and each

wave must satisfy the boundary condition that an exact number of its half-wavelengths must fit into the appropriate length b or c . The frequencies f of the normal modes are easily found from equation 9 by writing $f = \frac{v}{\lambda}$.

$$f^2 = v^2 \left(\frac{1}{\lambda^2} \right)$$

so
$$f^2 = \frac{v^2}{4} \left(\frac{m^2}{b^2} + \frac{n^2}{c^2} \right) \dots\dots\dots(11)$$

Each pair of values of m and n corresponds to one normal mode. As an example of the use of equation 11, let $c = \frac{1}{2}b$.

Thus
$$f^2 = \frac{v^2}{4} \left(\frac{m^2}{b^2} + \frac{4n^2}{b^2} \right) = \frac{v^2}{4b^2} (m^2 + 4n^2)$$

Writing
$$\frac{v^2}{4b^2} = f_0^2 \text{ for short,}$$

$$f^2 = f_0^2 (m^2 + 4n^2) \dots\dots\dots(12)$$

From equation 12, all the frequencies can be expressed as multiples (not usually integral multiples) of f_0 , for different values of m and n . Table 1 shows some of the values of f^2 in units of f_0^2 —i.e. only the values of $(m^2 + 4n^2)$ are shown, from which f can easily be found using equation 12.

Table 1 Relative values of f^2 for a rectangular membrane with $c = \frac{1}{2}b$

		<i>m</i>						
		1	2	3	4	5	6	7
<i>n</i>	1	5	8	13	20	29	40	53
	2	17	20	25	32	41	52	65
	3	37	40	45	52	61		
	4	65						

(Only values up to 65 are shown)

For example the ringed 20 in the fourth column indicates that for $n = 1, m = 4$

$$f^2 = 20 f_0^2$$

so
$$f = \sqrt{20} f_0$$

Note that, although the frequency can always be expressed as a multiple of f_0 , the fundamental (lowest) frequency ($m = 1$ and $n = 1$) is $\sqrt{5} f_0$, and *not* f_0 . The frequencies are not usually integral multiples of f_0 , nor of the fundamental frequency. Contrast this with the rope waves (on p. 13) for which all normal mode frequencies are integral multiples of the fundamental frequency.

In certain cases two different normal modes may have the same frequency; two such pairs have been ringed:

$$\begin{aligned} m=4, n=1 \text{ and } m=2, n=2 \text{ both have } f^2 &= 20f_0^2, \\ m=2, n=3 \text{ and } m=6, n=1 \text{ both have } f^2 &= 40f_0^2. \end{aligned}$$

Can you see two more pairs of normal modes having the same frequency?

When two or more normal modes have the same frequency, that frequency is called *degenerate*. The order of the degeneracy is equal to the number of normal modes sharing the frequency; the two examples mentioned above are therefore of order 2. There is no restriction to two states being degenerate; the degeneracy may have a higher order. For example the following three normal modes all have the same frequency $f = \sqrt{200} f_0$:

$$m=14, n=1; m=10, n=5; m=2, n=7.$$

This frequency therefore is degenerate with order 3. The concept of degeneracy is a very wide one and can be applied to any two parallel sets of information (frequency and normal mode in this case) where the correspondence is not simply one-to-one between them. Thus the genetic code (Unit 17, section 17.10) is degenerate; the two parallel sets are:

- (1) the groups of three bases in a particular order, and
- (2) the amino acids which are coded by the groups of bases.

The code is degenerate because a particular amino acid may be coded by more than one group of three bases. For example the amino acid leucine is represented by six different groups of bases: UUA, UUG, CUU, CUC, CUA and CUG where U is uracil, A is adenine, G is guanine and C is cytosine. This degeneracy is therefore of order 6.

The various modes of a rectangular membrane can be represented diagrammatically as in Figure 10(a). The shaded areas are 'up' when the unshaded areas are 'down' and vice versa. The lines between shaded and unshaded areas are nodal lines; notice that in two dimensions nodal lines replace nodes. Figure 10(b) shows what the membrane actually looks like at some instant in the $m=3, n=2$ mode, in case you have difficulty visualizing what is meant by the diagrams in Figure 10(a)

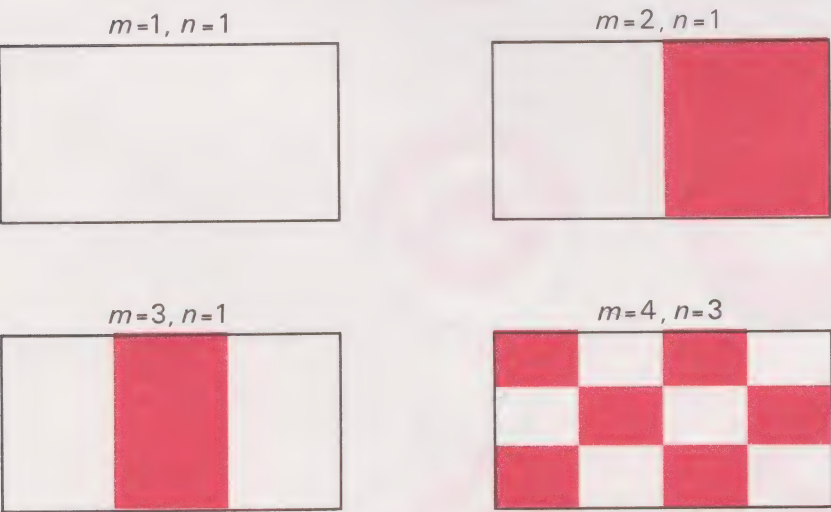


Figure 10(a) Some normal modes of a rectangular membrane.

The membrane is, of course, vibrating continuously so that the up-regions become down-regions half a cycle later.

- (1) $m=6, n=2$, and $m=4, n=3$ both have $f^2 = 52f_0^2$,
- (2) $m=7, n=2$, and $m=1, n=4$ both have $f^2 = 65f_0^2$.

degeneracy

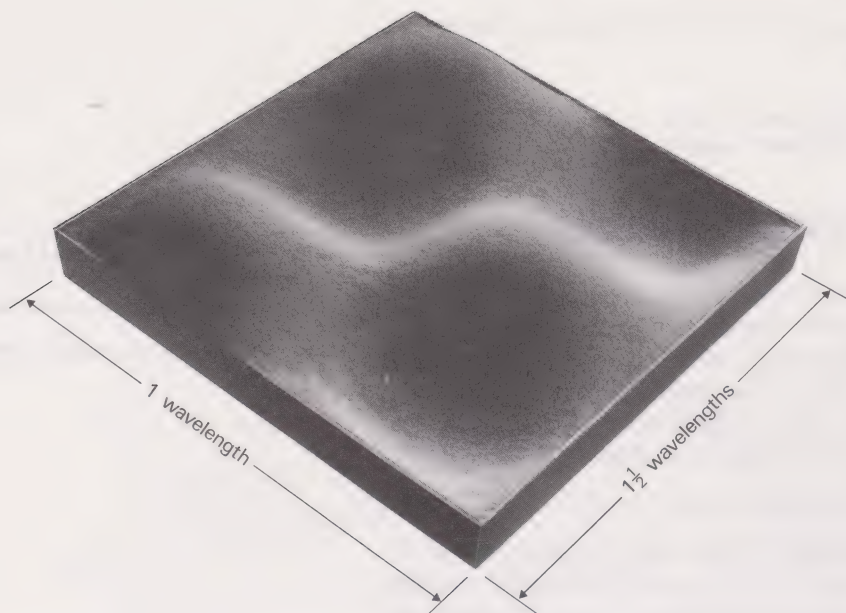


Figure 10(b) A sand model of the $m=3, n=2$ normal mode of a rectangular membrane.

10.3.2 Waves on a circular membrane

Because the force exerted by the nucleus on the electron has the same value all over the surface of a sphere centred on the nucleus, a hydrogen atom is spherical (in its ground state anyway) rather than rectangular or square. It is therefore useful to look briefly at the normal modes of a circular membrane, as the two-dimensional equivalent of a sphere. Some of these are shown diagrammatically in Figure 11 and as photographs in Figure 12. You will see them demonstrated in the TV programme.

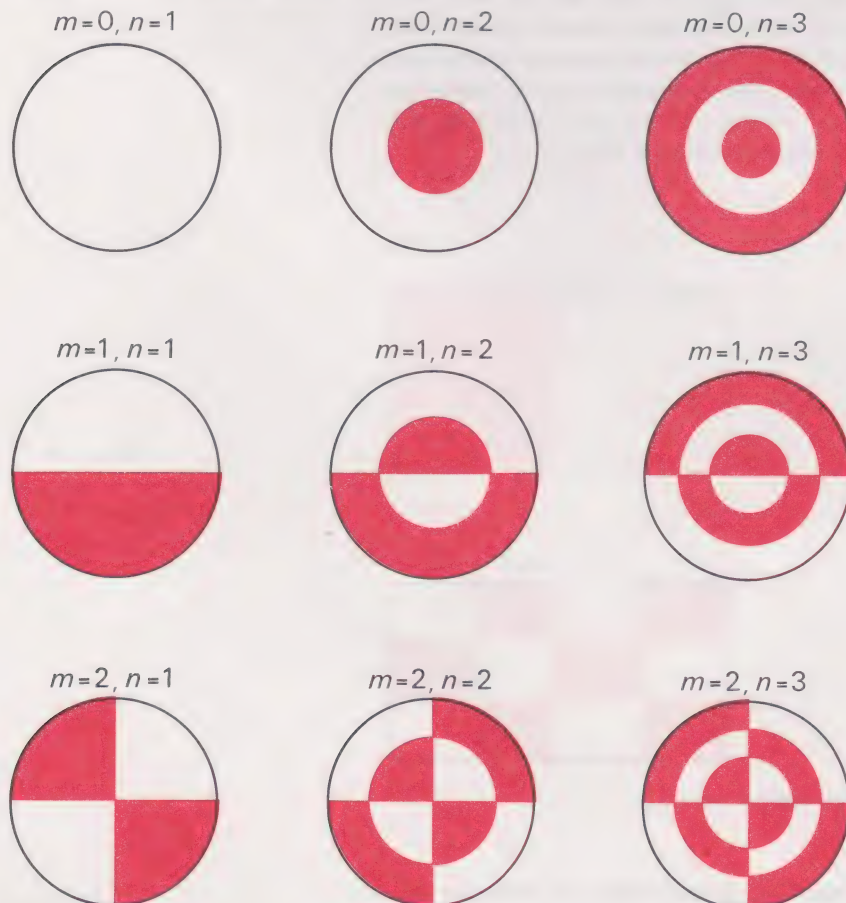


Figure 11 Some normal modes of a circular membrane.

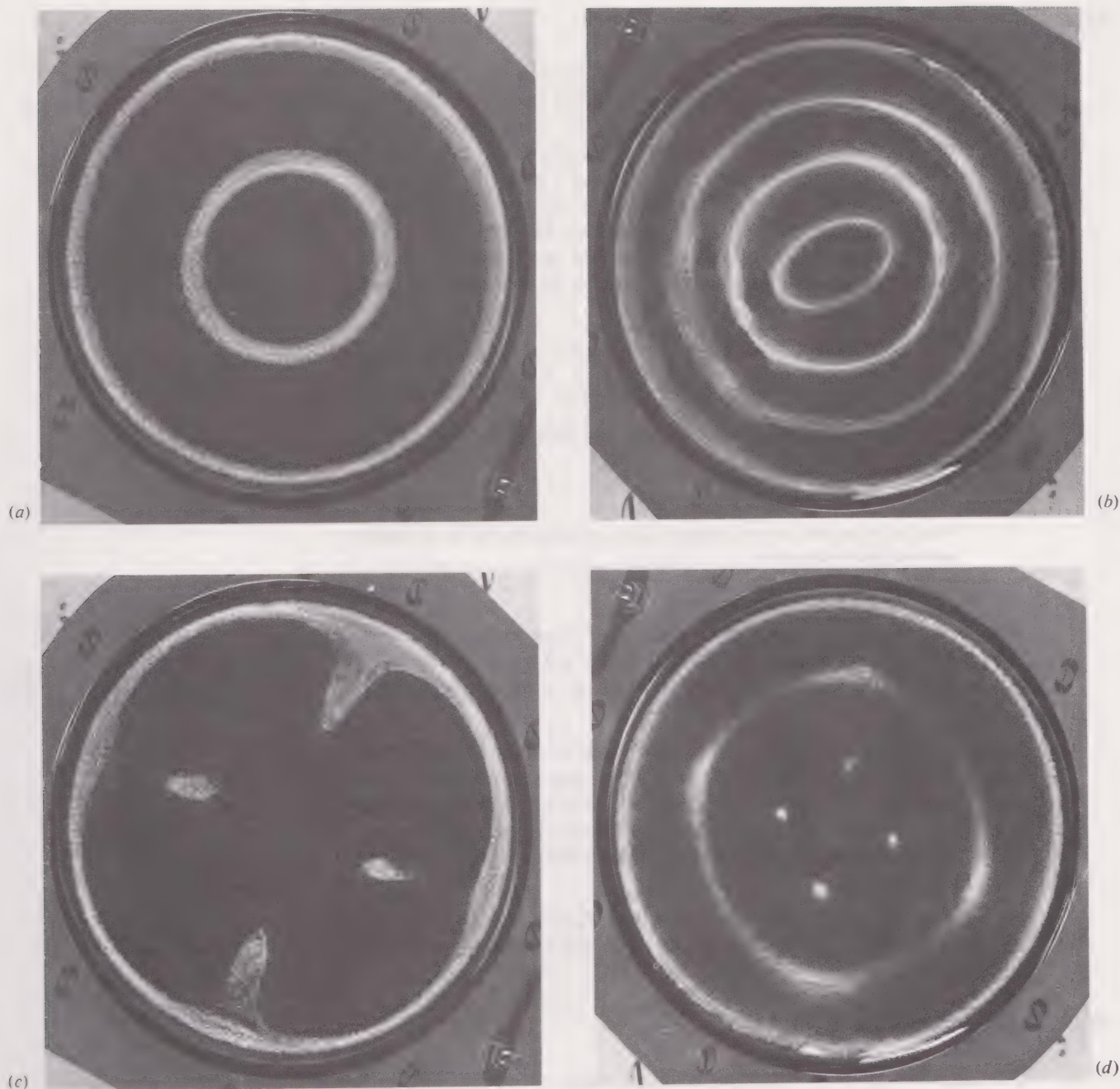


Figure 12 Photographs of a circular membrane vibrating in various normal modes. The membrane has been sprinkled with salt which tends to collect along the nodal lines. The nodal diameters of modes with $m \neq 0$ are not always very clear because of $m \neq 0$ modes with very similar frequencies, but you should be able to identify all the modes shown.

The quantum number n is now associated with radial division of the membrane surface, whereas m determines the division by diameters into sectors. Notice that n starts from one but m starts from zero, since n is equal to the number of nodal circles including the boundary, whereas m is equal to the number of nodal diameters. The frequencies of a circular membrane are not degenerate, but at higher values of m and n some may be so close as to be almost indistinguishable in practice.

The sound produced by any particular drum depends on the relative strengths of the normal modes excited when it is struck. These in turn are largely determined by where the drum is struck. For example, a blow in the centre would be unlikely to produce normal modes with m greater than zero since these modes all have nodal diameters through the centre.

30.3.3 Electron confined in two dimensions

The confinement of electron radiation in two dimensions, while leaving it unrestricted in position in the third, means that two pairs of parallel reflecting planes are needed (Fig. 13). As in the one-dimensional case (section 30.2.2), we deliberately sacrifice all knowledge of the electron's position measured at right-angles to the plane of Figure 13. This means that the momentum of the electron in that direction can be specified as zero without infringing Heisenberg's Uncertainty Relation; the velocity is then directed in the plane of Figure 13. Again this is only a thought-experiment, but very helpful as a stepping stone to the concept of complete confinement in an atom.

Possible values of momentum and kinetic energy are found exactly as in section 30.2.2 using the de Broglie formula (equation 4) and $T = \frac{p^2}{2m_e}$ (equation 5). However, the wavelengths are now given by equation 9 on p. 21, instead of equation 2.

Find an expression for the possible values of kinetic energy of an electron confined in two dimensions.

In a similar way the energies of an electron moving in two dimensions and confined by a circular boundary can be worked out from the theory of a circular membrane—though we have not given you enough theory to do it.

By analogy with a membrane, the energy levels of an electron confined between two pairs of parallel planes may be degenerate (two or more states, each with its own pair of quantum numbers, having the same energy), depending on the relative spacings of the planes, but the energy levels of an electron moving in two dimensions within a circular boundary are not degenerate.

Whatever the shape of the two-dimensional boundaries, two quantum numbers are needed to specify the state, and therefore the energy, of an electron confined in two dimensions.

30.3.4 Summary of section 30.3

The extension of the theory of confined waves from one into two dimensions introduces two new ideas. The first of these is that two quantum numbers are needed to specify a particular normal mode of a vibrating membrane or the state of a confined electron. The frequencies of the normal modes of a membrane are not integral multiples of a fundamental frequency like those of rope waves.

The second idea is a new concept—that of degeneracy. A frequency is degenerate if it can be produced by more than one normal mode (each mode being determined by a pair of quantum numbers). The frequencies of a rectangular membrane may be degenerate, depending on the ratio of the sides of the membrane. The frequencies of a circular membrane are not degenerate. Similarly the energy levels of electron radiation confined between two pairs of parallel planes may be degenerate, but those of electron radiation confined in two dimensions within a circular boundary are not degenerate.

Now do Self-Assessment Questions numbers 8 and 9 (p. 52).

For further reading on sections 30.2 and 30.3 see:

A. V. Baez, *The New College Physics—a Spiral Approach*, Chapters 16 and 17. Freeman, 1967.



Figure 13 Electron radiation is considered to be confined in two dimensions between two pairs of parallel planes.

$$T = \frac{h^2}{2m_e} \left[\left(\frac{m}{2b} \right)^2 + \left(\frac{n}{2c} \right)^2 \right]$$

where $m = 1, 2, 3 \dots$
and $n = 1, 2, 3 \dots$

If you had difficulty in obtaining this expression turn to Appendix 2 (Red).

30.4 Waves in Three Dimensions

The extension of wave theory from two into three dimensions follows exactly the same pattern as that from one into two, and you will probably not be particularly surprised at the results. Again, to make it easier, we want you first to think briefly about some waves which you can actually see. Then, as before, the results will be carried over to an electron in a similar situation.

30.4.1 Jelly waves in a rectangular box

Imagine a jelly which completely fills a glass-sided box. The jelly can vibrate (or wobble) inside the box. You can see the vibrations by watching the motion of something embedded in the jelly.

Look back at equations 10 and 9 for the normal mode wavelengths of one-dimensional waves and rectangular two-dimensional waves. Now try to guess the answers to the following questions by extrapolating† the earlier ideas.

How many quantum numbers are necessary for waves in three dimensions?

Three.

Write down by analogy with equations 10 and 9 an expression for the possible wavelengths λ of the normal modes of jelly waves in a rectangular box having sides of length a , b and c .

You should have written

$$\frac{1}{\lambda^2} = \left(\frac{l}{2a}\right)^2 + \left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2c}\right)^2 \dots\dots\dots(13)$$

where l , m , n are integers (quantum numbers).

It doesn't matter, of course, what letters you used for them, but THREE quantum numbers are needed. This is because there are three pairs of opposite faces in a three-dimensional box. The jelly wave which bounces around inside the box can be separated into three component-waves, one between each pair of opposite faces. Each of these component-waves must obey the usual boundary condition that an integral number of its half-wavelengths must fit between the faces, and this gives rise to three separate quantum numbers.

The boundary conditions for a jelly in a box are caused by the jelly being stuck to the walls so that the wave has a node all over the six faces of the box. Just as the lowest frequency mode of a rectangular membrane has the two quantum numbers (m and n) equal to 1, so the lowest frequency of jelly wave in the box will have all three quantum numbers equal to 1—each component wave has just one half-wavelength between its two boundaries.

30.4.2 Electron confined in a rectangular box—a simple model of an atom

The derivation of energy levels for electron radiation in a box will not be worked out in detail since it follows precisely the two-dimensional version of Appendix 2 (Red), but using equation 13 instead of equation 9; the only difference is an extra term which is carried right through to give the following expression for the kinetic energy T of the electron:

$$T = \frac{h^2}{2m_e} \left[\left(\frac{l}{2a}\right)^2 + \left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2c}\right)^2 \right] \dots\dots(14)$$

where $l = 1, 2, 3, \text{etc.}$
 $m = 1, 2, 3, \text{etc.}$
 $n = 1, 2, 3, \text{etc.}$ } quantum numbers.

This expression can be compared with equation 7 on p. 18 and with the answer to the question on p. 26. If, for example, l and m are both made equal to zero in equation 14 (which is equivalent to removing the boundaries in two of the dimensions), then equations 7 and 14 become identical.

Why do atoms have diameters of about 100 pm (see Unit 6, section 6.1.2) and not something very much smaller or larger? This cannot be answered in a few lines; the remainder of this section will concentrate on this very important problem, applied specifically to the hydrogen atom. We shall answer the question by using the wave theory of electrons to calculate a value for the diameter of a hydrogen atom in its lowest energy state.

The total energy of the single electron in a hydrogen atom is partly kinetic and partly potential energy. The kinetic energy may be obtained by regarding the atom as a cubical box having sides of unknown length. Of course the atom is actually spherical, and the electron is not confined by walls but rather by the electrical attraction of the nucleus. Nevertheless, for an order-of-magnitude calculation in which a diameter is only required within a factor of about ten, it is sufficient (and much easier) to liken the atom of radius r to a cubical box of side $2r$. The kinetic energy of the electron is then given by equation 14. Setting $l=m=n=1$ for the state of lowest energy, and $a=b=c=2r$:

$$T = \frac{h^2}{2m_e} \left[\left(\frac{1}{4r}\right)^2 + \left(\frac{1}{4r}\right)^2 + \left(\frac{1}{4r}\right)^2 \right]$$
$$\therefore T = \frac{3h^2}{32m_e r^2} \dots\dots\dots(15)$$

This expression shows correctly how the kinetic energy T of the electron depends on r , and also gives a correct order-of-magnitude value for the kinetic energy.

The potential energy between two charges Q_1 and Q_2 separated by a distance R was given in Unit 4, p. 29, equation 17.

$$PE = \frac{Q_1 Q_2}{4\pi\epsilon_0 R}$$

where ϵ_0 is the permittivity of empty space.

If $Q_1 = -q$ for the electron,
then $Q_2 = +Zq$ for the nucleus

(the atomic number Z is 1 for hydrogen, but its inclusion allows the result to be applied more generally).

So the potential energy of a single electron at a radius r is given by:

$$PE = - \frac{Zq^2}{4\pi\epsilon_0 r} \dots\dots\dots(16)$$

The kinetic and potential energies are shown in Figure 14 together with the total energy (in red) which is equal to their sum. You should understand that the values of total energy of an electron are being compared for different radii to find which radius the atom is likely to have. A given electron will, of course, have a constant total energy.

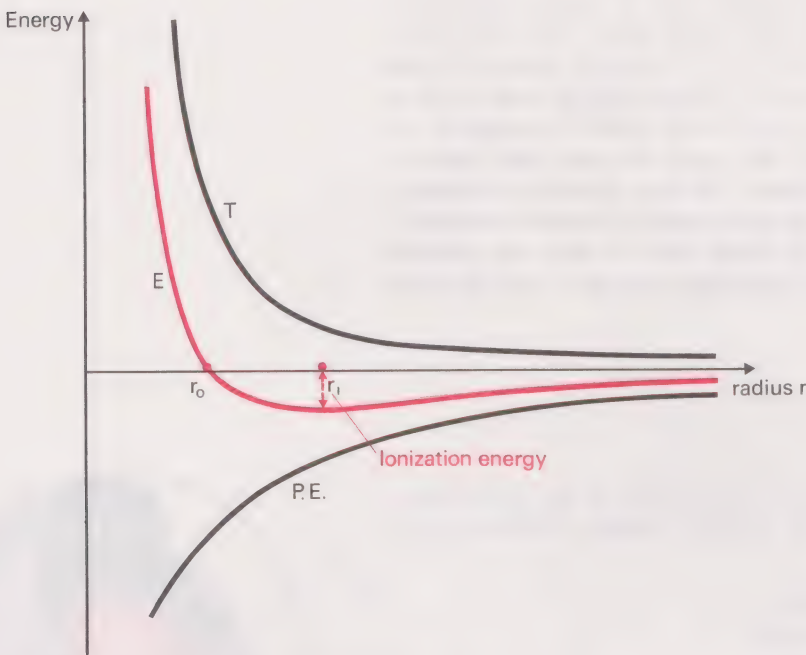


Figure 14 Energy of an electron in a hydrogen atom.

Don't be alarmed at the negative value for the potential energy. The zero value of potential energy is always quite arbitrary since all that ever matters is how potential energy changes with position. The important point is that the potential energy gets less as the electron approaches the nucleus. We have, for mathematical convenience only, chosen the zero level of potential energy to be the value when the electron is very far from the nucleus; it follows that the potential energy is negative at all closer positions.

The total energy has a minimum value at a radius r_1 . This happens because the kinetic and potential energies depend differently on r (equations 15 and 16). The atom will have a stable size with radius r_1 ; at any other radius it can release energy by changing its radius towards this value, r_1 can easily be found from the kinetic and potential energies. The derivation is given in Appendix 6 (Black) and leads to a result:

$$r_1 \approx \frac{h^2 \epsilon_0}{m_e Z q^2} \dots \dots \dots (17)$$

This will be the distance from the nucleus at which the electron will be found most often and may be equated with the radius of the atom. All the quantities on the right-hand side of equation 17 are constants, so this equation gives a value for the approximate size of a hydrogen atom calculated only from electrical theory and electron wave theory. The great question is—‘Does it agree roughly with the measured value?’

Substitution of

$h = 6.6 \times 10^{-34} \text{ J s}$	(Planck's constant)
$\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ kg}^{-1} \text{ m}^{-3} \text{ s}^2$	(permittivity of empty space)
$m_e = 9.1 \times 10^{-31} \text{ kg}$	(mass of an electron)
$Z = 1$	(atomic number of hydrogen)
and $q = 1.6 \times 10^{-19} \text{ C}$	(magnitude of the charge carried by a proton or electron)
gives $r_1 \approx 10^{-10} \text{ m}$ or 100 pm.	

This corresponds to a value of 200 pm for the diameter, which is remarkably close to the measured value of 100 pm. The measured value is only approximate anyway, and a factor of 2 is not significant in an order-of-magnitude calculation. So the wave theory of an electron leads automatically to a value for the diameter of a hydrogen atom which is consistent with the observed value. This is a major triumph for the quantum (wave) theory, for more precise calculations lead to perfect agreement. Further, there is no reason to expect a significantly larger value of diameter for atoms of much greater atomic number. For example, wherever there is a single outer electron, it moves around a region having a net positive charge (positive nuclear charge less negative inner electron charge) of +1 unit, just like the hydrogen atom. To the extent that this outer electron does not penetrate or approach too closely the inner electrons, the theory above (with $Z=1$) is still valid and the same atomic diameter is obtained. For an ion such as He^+ or Li^{++} , in which there is only one electron anyway, the theory is as correct as for hydrogen, though Z must be made equal to 2 or 3 respectively.

30.4.3 Electron confined in a hollow sphere

A hollow sphere obviously provides a better model of an atom than a cubical box because it has the same spherical shape. Three quantum numbers are still needed:

- n the principal quantum number
- l the azimuthal† quantum number
- m the magnetic quantum number

Perhaps you already recognize the nomenclature. Two of these quantum numbers (n and l) are the SAME ones that you met in Unit 7. At last we are coming near to explaining why there are quantum numbers for an atom, and how they are related to the energy level diagrams you studied so long ago (like Figure 10 in Unit 7). The electron wave function (i.e. the stationary electron wave) now occupies three dimensions, and the three quantum numbers determine the number of distinct regions into which the wave function is separated. Look back again to the two-dimensional waves shown in Figure 11 of this Unit (p. 24). In it the quantum numbers n and m determine the number of separate regions having nodal lines between them. In three dimensions, regions must be separated by surfaces, such as spheres. These nodal surfaces will be places on which an electron is not likely to be found. In Figure 11, the quantum number n is equal to the number of nodal circles (including the boundary), and the quantum number m is equal to the number of nodal diameters. In three dimensions, the relationship between quantum numbers and nodal surfaces is more complicated. There are two shapes of nodal surface:

- (1) concentric spheres—see Figure 15(a),
- (2) cones (with apex at the centre of the sphere)—see Figure 15(b).

Both kinds of nodal surface can, of course, be present simultaneously. Largely for historical reasons the numbers of nodal surfaces are related to the quantum numbers as follows:

- (1) there are $(n-l)$ nodal spheres, including the outer boundary.
- (2) there are $(l-|m|)^*$ nodal cones, including the equatorial plane (see Fig. 15(b)).

Being basically just a counting system, the relationship is really arbitrary,

* $|m|$ means the positive value of m , whether m is positive or negative—see MAFS Glossary.

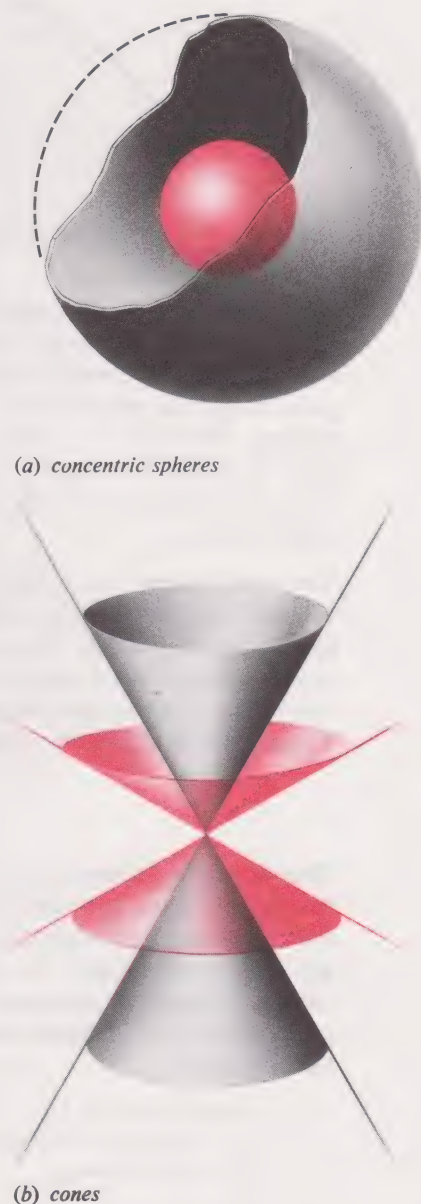


Figure 15 Nodal surfaces of an electron wave in a sphere.

but it is actually more sensible than it looks, for it leads to a very logical series of energy levels in the hydrogen atom as you will see in section 30.5.1.

You will probably have noticed that the two statements above are not sufficient to determine n , l and m , even when the details of the nodal surfaces are known. For example, suppose there are 3 nodal spheres and 2 nodal cones. If m is 0, then l is 2 and n is 5. But if m is 3, then l is 3 and n is 6; m could in fact be given any value. The two statements about the number of nodal surfaces are equivalent to fitting waves into two of the dimensions; the third piece of the puzzle is still missing. Fitting waves into the third dimension does not lead to nodal surfaces. The reason for this will unfortunately remain unclear to you; it is connected with the footnote on p. 17 and with a concept called complex numbers. Nevertheless, although no nodal surfaces can be distinguished, the quantum number m is associated with fitting waves into the sphere in a third dimension. Unlike n and l it can take positive, zero or negative (but always integral) values. Those of you who decide to study Physics further will come to understand the physical significance of m in later Courses. In this Foundation Course it is not possible to justify all the statements we have made about m .

Armed with this information, certain deductions can be made about the possible values of n , l and m .

The number of nodal cones is $(l - |m|)$. What can you deduce about the possible integral values that l can have?

Now turn to Unit 7, section 7.2.1. The rule for the values of l is set out there. You should see that it follows quite naturally from quantum theory. The values of m for any given value of l range from $-l$ through zero to $+l$ since l can never be less than $|m|$. For example, if $l=2$, m can be -2 , -1 , 0 , $+1$ or $+2$, making five distinct states.

The number of nodal cones must be zero or positive; you cannot have a negative number of them! Therefore $(l - |m|)$ must be zero or positive. Since m is unrestricted in value, l can be 0, 1, 2, 3, etc., but never less than $|m|$.

The number of nodal spheres is $(n - l)$. What can you deduce about the possible integral values that n can have?

Now turn again to Unit 7, section 7.2.1. You will find another rule for l —that it can take values up to a maximum of $(n - 1)$; in other words l must always be less than n . Again you have seen that this is a perfectly natural consequence of quantum theory.

The number of nodal spheres (including the outer boundary) cannot be less than one, so n must always be at least one greater than l . Since l can be 0, 1, 2, 3, etc., n can be 1, 2, 3, 4, etc., but n is always greater than l .

Section 30.4 is in many ways the most important section in this Unit. Although wave theory has not yet been applied formally to the hydrogen atom, most of the significant ideas have now emerged. There are two really important parts of this section. The first is the model of a hydrogen atom (section 30.4.2) in which the correct size of an atom is deduced. The second (section 30.4.3) introduces the major quantum numbers and the restrictions on their values. Study these parts very carefully and make quite sure that you understand the arguments presented. Then turn to the Self-Assessment Questions and do numbers 10 and 11 (p. 53). We have not included a formal summary of section 30.4, because it would be difficult to condense the arguments significantly without detracting from them.

30.5 Electron Waves in Atoms

An electron confined in an atom is very similar in principle to an electron confined in a hollow sphere. There is, however, one crucial difference (apart from the size of the region).

Can you remember what this difference is?

The difference is in the way of confining the electron. In a sphere, the electron is imagined to be confined by a hypothetical rigid wall and there is therefore in principle no upper limit to its possible energy—it will still be confined. An electron in an atom is confined only by an attractive force due to the nucleus, just as you are confined to the Earth's surface by gravity. If you are given too much kinetic energy you will escape from the Earth into space; similarly an electron with too much energy will escape from its nucleus leaving the atom ionized. If the zero of potential energy is taken to be the level a long way from the nucleus (as in this Unit—see Fig. 14 and equation 16), then a bound electron must have a negative total energy—zero total energy would just allow it to escape. There is an upper limit of zero to the energy which an electron may have and still be part of an atom. The condition that the wave function must fall rapidly to zero at large distances (so that there is a negligible probability of finding the electron a long way from the nucleus) replaces the outer boundary condition of a nodal surface for a hollow sphere. It leads in the same way to a principal quantum number n taking only whole-number values.

You may be wondering how this scale of energy can be reconciled with Unit 6 (section 6.5), where the energy of an electron in the ground state of hydrogen is taken to be zero. There is no contradiction because the zero of potential energy is completely arbitrary. In Unit 6 this zero is deliberately chosen to make the electron's total energy zero in the ground state, but in this Unit it is more convenient to have a different zero level.

30.5.1 Energy levels of hydrogen

The actual calculation for hydrogen is, of course, quite tricky—more so than the case of the hollow sphere.

Can you see why this should be so?

It has been assumed that an electron in a hollow sphere has a constant momentum and kinetic energy. In an atom this is not true. Only the total energy is a constant for a particular state of the electron, but both its potential energy PE and its kinetic energy T depend on its distance r from the nucleus. Proper calculations must take into account that with increasing r :

- | | | |
|--|---|----------------------------|
| <ul style="list-style-type: none"> (1) the potential energy increases (2) the kinetic energy T decreases (3) the momentum p decreases (4) the wavelength $\lambda(=h/p)$ increases. | } | $PE + T = \text{constant}$ |
|--|---|----------------------------|

The full calculation was first performed in 1926 by Erwin Schrödinger; the results are sufficiently straightforward to be understood without wading through the mathematics. An energy level can be calculated for each value of n , l and m . It turns out that the value of m does not affect the result (except in the presence of a magnetic field; hence the name of that quantum number). The energy levels for hydrogen, calculated from this theory, are shown to scale in Figure 16

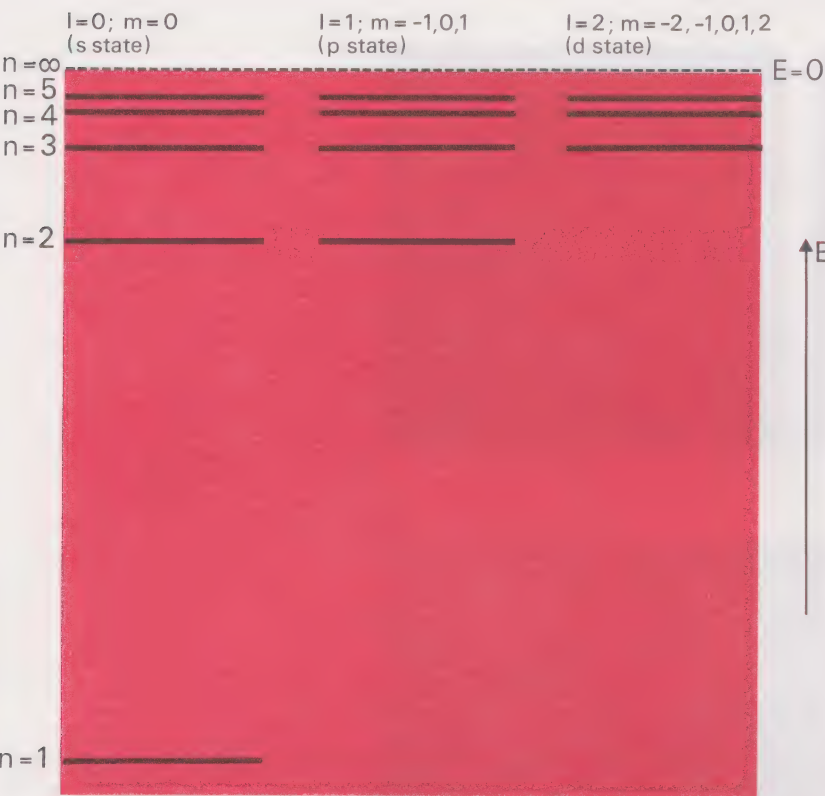


Figure 16 Energy levels of the hydrogen atom.

It is evident that the total energy E depends only on a single quantum number n (the principal quantum number). When n is fixed, the energy levels corresponding to all possible values of l and m coincide. Thus the energy levels of the hydrogen atom (except the lowest) are highly degenerate, because several different electron states (described by different combinations of l and m) have the same energy. You should now see that, although the quantum numbers seemed to be specified in a rather odd way on p. 30, the effect is to produce a very rational scheme of energy levels. When an electron changes from a higher to a lower energy level, the surplus energy ΔE is radiated in the form of a quantum of electromagnetic radiation called a photon, the frequency f being given by:

$$\Delta E = hf \dots\dots\dots(18)$$

where h is Planck's constant (see Unit 29, section 29.2.2).

The frequencies calculated from Figure 16, using equation 18, are in complete agreement with the frequencies observed in the atomic spectrum of hydrogen (Fig. 17).

Because the energy levels are fixed, an atom can never 'wear out'. The energy levels for a given kind of atom are always the same, and hence the frequencies of spectral lines never change. It is this property that makes the frequencies and wavelengths of spectral lines so suitable for universal standards of time and length—see Unit 2, section 2.4.2. The success of this explanation of the hydrogen spectrum is a considerable triumph for

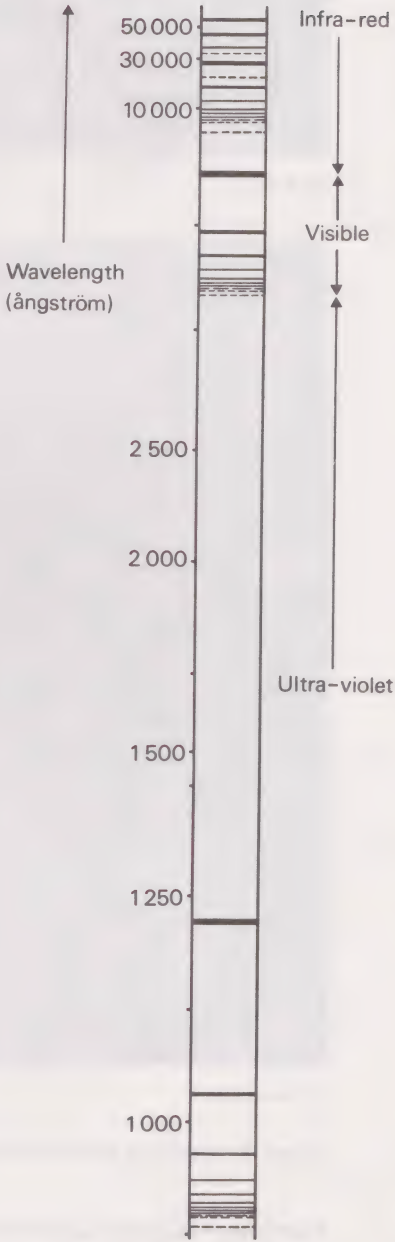


Figure 17 Spectrum of the hydrogen atom. (A colour reproduction of this spectrum can be seen on the cover of Unit 6.)

quantum theory. It does not prove that the theory is right, for another theory might also be able to explain the experimental results, but it is nevertheless a major achievement.

30.5.2 Shapes of electron states in hydrogen

An impression of the distribution of electron probability ψ^2 for hydrogen in various states with $l=0$ is shown in Figure 18. The shading is most intense where the electron is most likely to be.

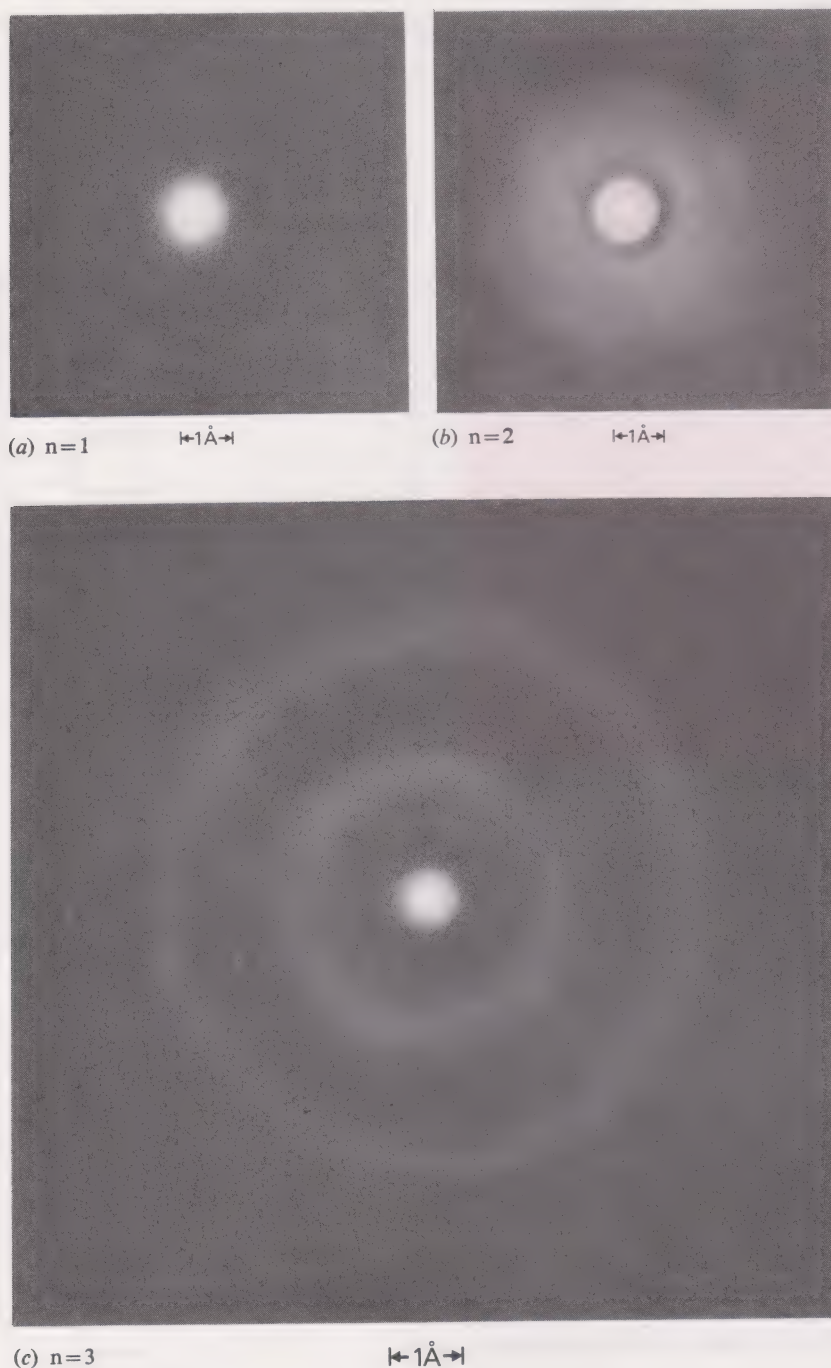


Figure 18 Shapes of hydrogen electron states with $l=0$.

Remember that, because of the uncertainty principle, any question about the precise location of the electron is not meaningful. There is a probability assigned to all the various possible positions and Figure 18 shows the distribution in space of this probability.

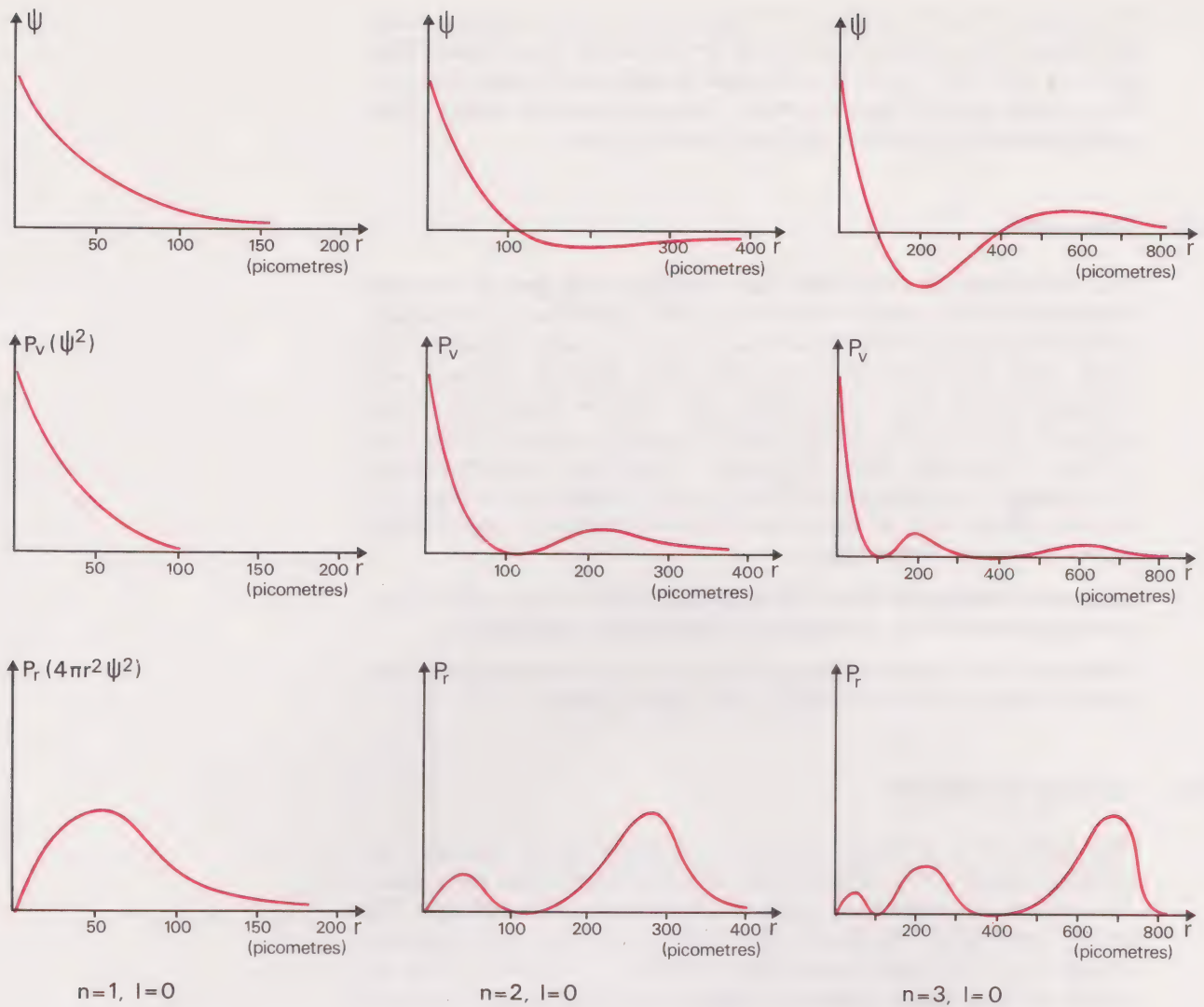


Figure 19 Electron wave functions and probabilities in the hydrogen atom; the radius is in picometres.

States with $l=0$ have a spherically symmetric distribution. Notice that in the $n=1$ state the electron is more likely to be in a region close to the centre (nucleus) than in any other region of the same volume. Because of this, electron capture by the nucleus does occasionally take place from this state in some atoms, though not in hydrogen. In the $n=2$ state there is a second spherical region, but the electron may still be found close to the nucleus.

It is important to distinguish between two different kinds of probability.

- (1) The probability P_v of finding the electron in a small volume of fixed size at a given distance r from the nucleus. Figure 18 shows this probability.
- (2) The radial probability P_r of finding the electron at a particular radius r —strictly of finding it in a thin shell of radius r and fixed thickness, like the rubber part of a squash ball.

Because a shell of fixed thickness t has a volume which increases as r^2 —its volume is $4\pi r^2 t$ —these two probabilities are not equal:

$$P_r = 4\pi r^2 P_v$$

The most obvious difference between P_r and P_v is that P_r is equal to zero when r is zero because the shell volume is then zero. Graphs of ψ , P_v and P_r are shown in Figure 19.

It is apparent from the graphs of P_r that there is a series of radii at which the electron has a higher-than-average probability of being found. Thus the $n=3, l=0$ state has three such radii, though one of these (the outer one) is more probable than the others. You may have seen graphs of the radial probability P_r before—in Unit 7, section 7.A2.4.

30.5.3 Other atoms

The wave theory of atoms other than hydrogen is in general extremely complicated since a complete picture must take account of the interactions of all the electrons present. Nevertheless, atoms in Group I of the Periodic Table, such as sodium and potassium, have much in common with hydrogen because each has a single outer electron. This electron does approach the inner ones and as a result its energy levels are not the same as those of hydrogen. There is, however, a significant similarity revealed by an energy level diagram equivalent to the hydrogen one in Figure 16, but the energy levels of states with the same value of n and different values of l are no longer equal.

Theoretical calculations have only been performed for the simpler atoms, but the agreement with spectral and other evidence is satisfactory.

When you have finished studying this section, try to summarize the main ideas in your own words; then read our summary below.

30.5.4 Summary of section 30.5

The theory of a hydrogen atom is complicated by the fact that the potential energy of the electron varies with its distance from the nucleus; this implies a corresponding variation of the electron's wavelength. The energy levels (Fig. 16) derived from the wave theory are degenerate (except the lowest one), because for each value of the energy there are several different states—remember, there are different values of m to be considered too.

The value of an energy level in the hydrogen atom depends only on the quantum number n . The spectra deduced from the energy levels are in complete agreement with experimental observations.

The position of an electron in an atom cannot be determined precisely—this is a consequence of Heisenberg's Uncertainty Relations. A probability can be assigned to each position and this measures the likelihood of finding the electron there. The radial probability is derived from this and measures the likelihood of finding the electron at a particular distance from the nucleus; this radial probability is characterized by a series of distances at which the electron is more likely to be found than at others (Fig. 19).

Atoms other than hydrogen are more complicated, but those in Group I of the Periodic Table have much in common with hydrogen because of their single outer electron.

You should now do the remaining Self-Assessment Questions (12, 13 and 14).

30.6 Summary of the Unit

When a rope is clamped at both ends under tension, a stationary wave can exist on it consisting of a wave being continually reflected between the two ends. The rope can vibrate with only certain discrete frequencies and wavelengths called normal modes, which are characterized by a single quantum number taking integral values. The momentum of an electron confined in one dimension (between two parallel planes) is related to the allowed wavelengths by the de Broglie formula, and this in turn leads to a series of discrete energy levels characterized by one quantum number.

In two dimensions, a membrane can vibrate with discrete frequencies and wavelengths which are determined by two independent quantum numbers. An electron confined in two dimensions therefore has energy levels determined by two quantum numbers.

Jelly waves in three dimensions require three quantum numbers to specify a particular normal mode in a box and the energy levels of an electron in such a box are similarly determined. The lowest energy level of the electron is called its zero-point energy. A simple model of a hydrogen atom in which this zero-point energy is combined with the electrical potential energy of the electron leads to the observed diameter of this atom.

An improved model of hydrogen takes proper account of the potential energy. This leads to a series of degenerate energy levels with three quantum numbers (n , l and m). These energy levels are consistent with the observed spectrum and other data. The various states of the hydrogen atom can be pictured in terms of probability density diagrams (like Figure 18) in which there are nodal surfaces on which the electron will not be found. The probability of finding an electron in any particular part of the atom depends on the value of the square of the wave-function there. Other atoms, such as sodium and potassium, in which there is a single outer electron have a series of energy levels closely related to those of hydrogen.

Background Reading

E. Huggins, *Physics One*, Chapter 16. W. A. Benjamin Inc., 1968.
A. V. Baez, *The New College Physics—a Spiral Approach*. W. H. Freeman & Co., 1967.

Electron Confined in One Dimension

In section 30.2.2, an expression is obtained (equation 7) for the possible values which can be taken by the kinetic energy of an electron confined in one dimension between two parallel planes. Although this may seem a rather artificial example, the extension to three dimensions does not change the basic idea of a series of discrete energy values (or energy levels).

The starting point is equation 2, giving the wavelengths that will fit into the box:

$$\lambda = \frac{2c}{n} \text{ where } n=1, 2, 3, \text{ etc. } \dots (2)$$

The wavelength of an electron probability wave is not directly observable and the de Broglie formula (equation 4) is used to write down the momentum:

$$p = \frac{h}{\lambda} \dots\dots\dots (4)$$

Finally the kinetic energy T is obtained from the standard expression valid for velocities much less than that of light:

$$\begin{aligned} T &= \frac{1}{2} m_e v^2 \quad (\text{Unit 4, equation 25}) \\ &= \frac{1}{2} \frac{(m_e v)^2}{m_e} \\ T &= \frac{p^2}{2m_e} \dots\dots\dots (5) \end{aligned}$$

since the momentum p is equal to $m_e v$.

The derivation of the energy levels consists of combining equations 2, 4 and 5. Instead of starting from the expression for the kinetic energy (equation 5) and substituting the other two equations into it (as in the main text) the logic can be broken down into steps which may make it clearer:

$$\lambda = \frac{2c}{n}$$

Equation 2

$$p = \frac{h}{\lambda}$$

Equation 4

$$= \left(\frac{n}{2c} \right) h$$

$$= \frac{nh}{2c}$$

Substitution of possible values of λ to obtain possible values of p , and rearrangement.

$$T = \frac{p^2}{2m_e}$$

Equation 5

$$= \left(\frac{nh}{2c} \right)^2 \left(\frac{1}{2m_e} \right)$$

$$= n^2 \left(\frac{h^2}{8c^2m_e} \right)$$

Substitution of possible values of p to obtain possible values of T and rearrangement to give equation 7.

Discrete values of the wavelength λ determined by the condition that an exact number of half-wave-lengths fit must into the box.

(4)

Discrete values of momentum p .

(5)

Discrete values of kinetic energy T (energy levels).

The result is a series of energy levels which, if expressed in units of size $\left(\frac{h^2}{8c^2m_e} \right)$, have values given by n^2 and therefore form a series 1, 4, 9, 16, etc.

These levels are plotted vertically in Figure 9 (p. 19).

Electron Confined in Two Dimensions

The derivation of possible energies for an electron confined in two dimensions follows precisely the one-dimensional derivation of Appendix 1 (Red). The starting point is equation 9, giving the wavelengths that will fit into the box:

$$\frac{1}{\lambda^2} = \left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2c}\right)^2 \dots\dots\dots(9)$$

where $m = 1, 2, 3, \text{etc.}$
and $n = 1, 2, 3, \text{etc.}$ } quantum numbers.

The allowed values of momentum are found from the de Broglie relation

$$p = \frac{h}{\lambda} \dots\dots\dots(4)$$

and the values of kinetic energy from

$$T = \frac{p^2}{2m_e} \dots\dots\dots(5)$$

as in Appendix 1 (Red).

From equation 4, $\frac{1}{\lambda} = \frac{p}{h}$

Substituting $\frac{p}{h}$ in place of $\frac{1}{\lambda}$ in equation 9,

$$\left(\frac{p}{h}\right)^2 = \left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2c}\right)^2$$

Rearranging to obtain an expression for the allowed values of momentum p :

$$p^2 = h^2 \left[\left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2c}\right)^2 \right]$$

Now substitute this expression for p^2 into equation 5 to give the allowed energy levels:

$$\begin{aligned} T &= \left(\frac{1}{2m_e}\right)p^2 \dots\dots\dots(5) \\ &= \frac{h^2}{2m_e} \left[\left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2c}\right)^2 \right] \end{aligned}$$

where $m = 1, 2, 3, \text{etc.}$
and $n = 1, 2, 3, \text{etc.}$

This is the expression quoted in section 30.3.3. It may be compared with equation 7 on p. 18, for if m is made zero (corresponding to the removal of one pair of planes) the two expressions are the same.

Appendix 3 (Black)

Sound Waves

Sound waves consist of vibrations of air to and fro along the direction in which the wave is travelling. These give rise to regions of slightly higher and slightly lower pressure which are propagated through the air with a speed which, like that of the waves on a rope, does not depend on the frequency of vibration of the source. This must be true or very nearly so, because an orchestra sounds perfectly normal at the back of a concert hall whereas, if different frequencies (itches) travelled with different speeds, then by the time the sound waves reached the back of the hall the music would sound very odd indeed. The velocity does depend on temperature and slightly, in a tube, on the diameter of the tube. Under normal laboratory conditions the velocity of sound may be taken as 340 m s^{-1} , and variations from this value are not likely to exceed 1 or 2 per cent. The actual displacements of air molecules from their mean positions are relatively small; the faintest sound that can be heard by a human ear corresponds to a displacement of the air molecules through a distance equal to about one molecular diameter. Figure 20 shows the variation of the displacement with position at a fixed instant of time.



Figure 20 Displacement of air molecules from their mean positions in a sound wave of single frequency at a fixed instant of time.

The whole pattern travels to the right (along the x axis) with constant speed. Note that, although for graphical reasons the displacement is plotted at right angles to x , it still represents an actual movement in the same direction as x . This is an example of a *longitudinal wave* (see p. 9).

When two waves of the same amplitude and frequency but opposite direction are combined, a stationary wave pattern (like that on a rope) is formed (Fig. 21) though, of course, the nodes and antinodes are not visible to the eye.

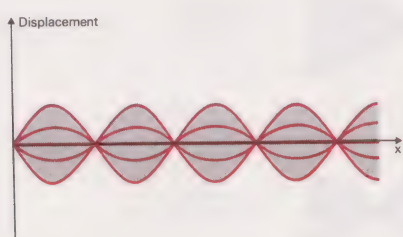


Figure 21 A stationary sound wave.

The shaded region is a 'time-exposure' of the graph which at any instant might be represented by one of the solid lines (including the x axis).

To determine the frequencies of the normal modes in a tube it is necessary to consider the boundary conditions at the two ends. At a closed end the air molecules cannot vibrate along the tube axis at all, so that point must always be a node. Most organ pipes and musical wind instruments have one closed end and one open end to the tube. A wave travelling along the tube is partially reflected back down the tube at the open end due to the change in propagation conditions and this gives rise to a stationary wave. Nevertheless, an appreciable amount of energy escapes continuously from the open end (which is, of course, the whole point of a musical instrument) and, unless this is replaced from a source of energy, the amplitude of the oscillations will quickly die down. Although the wave is partially reflected at the open end, there is no reason to expect a node there, for the air molecules are clearly free to vibrate along the axis in that region. Theoretical calculations show that an antinode of the displacement graph occurs near the open end; for an unflanged tube this is located a distance of about $0.6 r$ outside the end of the tube, where r is the radius.

The normal modes of sound waves in a tube open at one end can now be worked out quite easily using the boundary conditions that there must be a displacement node at the closed end and a displacement antinode near the open end. Sketch graphs of displacement in some of the modes are shown in Figure 22. Note that for simplicity the length c of the tube is assumed to include the end-correction of $0.6 r$ mentioned above. Thus c is measured from the node at the closed end to the antinode just outside the open end.

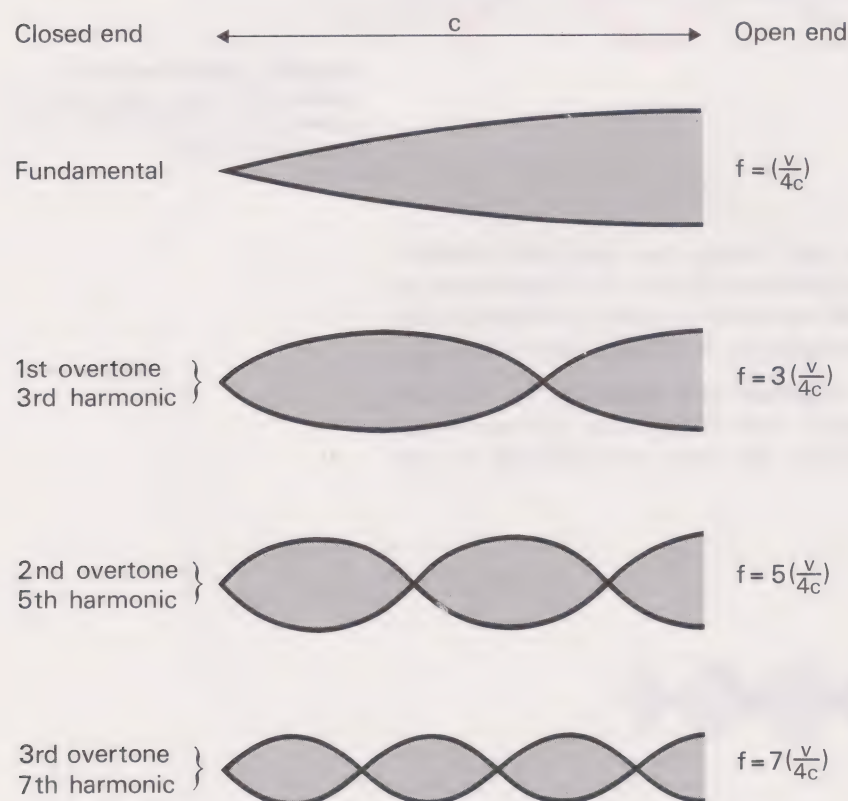


Figure 22 Normal modes in a tube open at one end only.

What is the shortest distance between a node and an antinode?

$\frac{1}{4}\lambda$

You have already answered this question in section 30.2.1, but this is where the answer is used. There can be any number of half-wavelengths as well, starting from the closed end, but there must be an odd quarter-wavelength to get from the last node to the final antinode at the open end.

$$\begin{aligned}\therefore c &= n\left(\frac{\lambda}{2}\right) + \frac{\lambda}{4} \\ &= (2n+1)\left(\frac{\lambda}{4}\right)\end{aligned}$$

and $\lambda = \frac{4c}{2n+1}$ where $n=0, 1, 2, 3, 4$, etc.

Note that n can be zero with the equation written this way.

Using $f = \frac{v}{\lambda}$ as before,

$$\begin{aligned}f &= \frac{v}{4c/(2n+1)} \\ \therefore f &= (2n+1)\left(\frac{v}{4c}\right) \dots\dots\dots(19)\end{aligned}$$

where $n = 0, 1, 2, 3$, etc.

This equation is used as the basis of the frequencies shown in Figure 22. There are certain important differences between the normal modes in a tube open at one end (equation 19), such as a trumpet, and those on a rope or wire clamped at both ends (equation 3), such as a violin string.

Is the relationship between overtone number and harmonic number the same in both cases?

No.

Compare Figures 4 and 22. On a rope clamped at both ends (and also in a tube closed at both ends) the harmonic number is always one higher than the overtone number. Remember, however, that they are defined in quite different ways (see p. 13). In a tube open at one end, the overtones are still (as always) numbered consecutively, but not all the harmonics can exist, so the harmonic number is *not* simply one greater than the overtone number.

Which harmonics are missing in a tube open at one end?

The even numbered harmonics (2nd, 4th, 6th, etc.) are all missing. Only the fundamental and its odd harmonics can exist (see Fig. 22).

Draw a sketch graph as in Figure 22 to show the 5th overtone for a tube open at one end and write down the frequency and wavelength in terms of the length c of the tube.

See Figure 23 for solution.

As with a vibrating rope, a typical vibration of the air in a tube will contain all possible normal modes with various relative amplitudes. The fact that only odd harmonics can exist in a tube open at one end will impart a different tone to a note from such a tube compared with a note 'leaked out' from a tube essentially closed at both ends.

The de Broglie Formula and Uncertainty

It was stated in Unit 29, section 29.4.1, that Heisenberg's uncertainty relations add nothing really new to the de Broglie formula. As a demonstration of this, take the derivation of the zero point energy T_1 given by equation 8 in section 30.2.2. This was obtained using the de Broglie formula $p = h/\lambda$. It is easy to show that this is consistent with the uncertainty relations. The uncertainty in position Δx must be the length c between the two planes confining the electron.

But $\Delta p_x \cdot \Delta x = h$ where Δp_x is the uncertainty in the x component p_x of the momentum p —Unit 29, equation 8.

$$\therefore \Delta p_x = \frac{h}{\Delta x} = \frac{h}{c}$$

The uncertainty in p_x may be interpreted crudely as due to the lack of knowledge about the direction of the electron's momentum p . Thus p_x can be $+p$ or $-p$ and so

$$\Delta p_x \approx 2p$$

$$\therefore p \approx \Delta p_x \approx \frac{h}{2c}$$

which corresponds to a kinetic energy T given by

$$T = \frac{p^2}{2m_e} \quad (\text{equation 5})$$

$$\approx \left(\frac{h}{2c}\right)^2 \left(\frac{1}{2m_e}\right)$$

$$\approx \frac{h^2}{8c^2m_e} \quad (\text{compare with equation 8})$$

This is not a derivation of the zero-point kinetic energy (equation 8), but it does show that the zero-point kinetic energy is consistent with the uncertainty relations. Do you now begin to see the equivalence of the two ideas?

The existence of a lowest non-zero kinetic energy may become clearer if you take the hypothesis that the electron has zero kinetic energy and follow through the consequences of it. Try this yourself before reading on.

If T is zero, p is also zero and therefore precisely known, so the uncertainty (Δp_x) in p is zero: $\Delta p_x = 0$.

But $\Delta x \cdot \Delta p_x = h$

$$\therefore \Delta x = \frac{h}{\Delta p_x} \rightarrow \infty$$

Δx is infinity. In other words the electron could be anywhere in the universe and we have absolutely no information about its location. Since the universe is infinitely larger (almost) than the space between the planes, there is a vanishingly small probability that this space contains an electron at all. But the electron is known to be in the space between the planes, so the original hypothesis that it has zero energy is untenable since it leads to a contradiction.

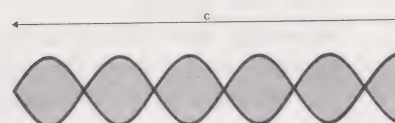


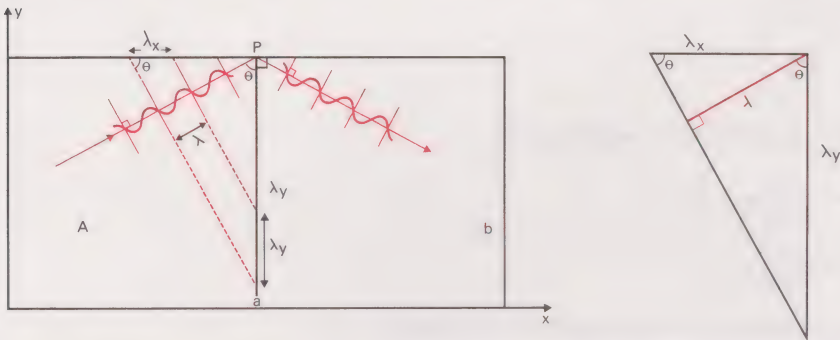
Figure 23 Fifth overtone of a tube open at one end only.

Appendix 5 (Black)

Normal Modes of a Rectangular Membrane

In this Appendix the theory behind equation 9 in section 30.3.1 is discussed.

Imagine a wave of wavelength λ (Fig. 24(a)) being reflected from a boundary of the membrane at some angle of incidence θ measured between the 'ray' AP and the normal to the boundary. The angle between a wave-crest (in red) and the boundary is also equal to θ .



(a) Reflection of a wave on a membrane. (b) Geometrical relationships.

Figure 24

Now think of the wave as two separate waves added together, one moving parallel to the x axis with wavelength λ_x and one moving parallel to the y axis with wavelength λ_y . To an observer at P with blinkers on so that he can only observe the motion parallel to the x axis, λ_x is given by

$$\left. \begin{aligned} \lambda_x &= \frac{\lambda}{\sin \theta} \\ \lambda_y &= \frac{\lambda}{\cos \theta} \end{aligned} \right\} \dots\dots\dots (20)$$

Similarly

For convenience, the geometric relation between λ , λ_x and λ_y is shown more clearly in Figure 24(b). If you are uncertain about the algebra refer to *MAFS*, section 4.A.1.

It is clear (Fig. 25) that a 'ray' can be reflected round the four boundaries and emerge in the same direction as it originally had, though not necessarily along the same path.

The wave-crests are at right-angles to the rays and can 'fill' the surface of the membrane, so the sideways shift of the ray is not important. A two-dimensional stationary wave is set up on the surface.

On a rope, the boundary conditions required a node at each end. On a membrane, there must be a node all round the perimeter; since the membrane is clamped all round. Treating the x wave and y wave separately and applying the same condition as on a rope,

c must be an exact multiple of $\frac{1}{2}\lambda_x$. This determines the possible values of λ_x .

What condition must b and λ_y satisfy?

b must be an exact multiple of $\frac{1}{2}\lambda_y$.

There are now two boundary conditions both of which must be satisfied:

$$\left. \begin{aligned} c &= n \frac{\lambda_x}{2} \\ b &= m \frac{\lambda_y}{2} \end{aligned} \right\} \dots\dots\dots(21)$$

where m and n are positive whole numbers not equal to zero and not necessarily equal to each other (though they may be). Of course b and c are actually fixed in value. It is λ_x and λ_y that must obey equation 21, so

$$\left. \begin{aligned} \lambda_x &= \frac{2c}{n} \\ \lambda_y &= \frac{2b}{m} \end{aligned} \right\}$$

Substituting from equations 20 for λ_x and λ_y into equations 21,

$$\left. \begin{aligned} c &= \frac{n \lambda}{2 \sin \theta} \\ b &= \frac{m \lambda}{2 \cos \theta} \end{aligned} \right\} \dots\dots\dots(22)$$

It will not in general be possible to satisfy both equations 22 simultaneously, except for certain values of θ . In order to find the waves that are possible on the membrane, eliminate θ between the two equations 22, using the relation:

$$\cos^2 \theta + \sin^2 \theta = 1$$

(See *MAFS*, section 4.C.3, if you do not know this relation.)

From equations 22,

$$\left. \begin{aligned} \cos \theta &= \frac{m \lambda}{2b} \\ \sin \theta &= \frac{n \lambda}{2c} \end{aligned} \right\}$$

$\therefore \left(\frac{m \lambda}{2b} \right)^2 + \left(\frac{n \lambda}{2c} \right)^2 = 1$
 or $\left(\frac{m}{2b} \right)^2 + \left(\frac{n}{2c} \right)^2 = \frac{1}{\lambda^2} \dots\dots\dots (9)$

This is the result used in section 30.3.1 from which the normal mode frequencies of a rectangular membrane are deduced.

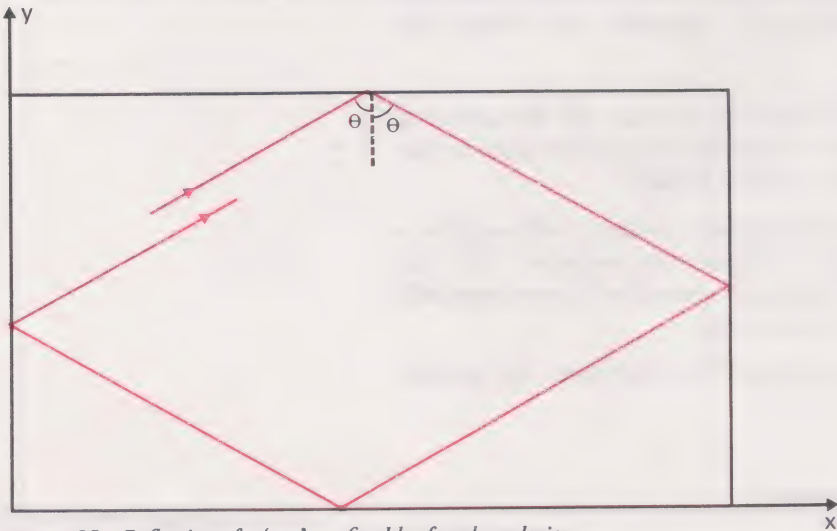


Figure 25 Reflection of a 'ray' confined by four boundaries.

Appendix 6 (Black)

Size of a Hydrogen Atom

In section 30.4.2, a graph was shown (Fig. 14) of the energy of an electron in a hydrogen atom, derived from the addition of the kinetic energy and potential energy. The value of the radius at the position of minimum total energy (equation 17) will now be derived. This is the approximate mean radius of the atom.

$$\text{Kinetic energy } (T) = \frac{3h^2}{32m_e r^2} \dots\dots\dots(15)$$

$$\text{Potential energy } (PE) = -\frac{Zq^2}{4\pi\epsilon_0 r} \dots\dots\dots(16)$$

Therefore the total energy E is

$$E = T + PE$$

$$E = \frac{3h^2}{32m_e r^2} - \frac{Zq^2}{4\pi\epsilon_0 r} \dots\dots\dots(23)$$

The problem is to find the value of r for which this expression is least— r_1 on Figure 14. This can easily be done by the methods of differential calculus. However, if you look at Figure 14, you will see that at a slightly smaller radius (r_0) the value of E is zero. r_1 and r_0 are clearly of the same order-of magnitude; one is not ten times the other. In fact r_1 is only twice r_0 and factors of this magnitude are not significant in an order-of magnitude calculation. Setting E equal to zero in equation 23 to find r_0 ,

$$\begin{aligned} \frac{3h^2}{32m_e r^2} &= \frac{Zq^2}{4\pi\epsilon_0 r_0} \\ \therefore r_0 &= \frac{12\pi h^2 \epsilon_0}{32m_e Zq^2} \end{aligned}$$

Dropping all numerical constants (including π) which roughly cancel and equating r_1 with r_0 ,

$$r_1 \approx \frac{h^2 \epsilon_0}{m_e Zq^2} \dots\dots\dots(17)$$

This is the result used in section 30.4.2 to find the approximate radius of a hydrogen atom.

Glossary

AZIMUTH The arc which extends in a vertical plane from directly above to directly below. Direction in this plane is specified by the angle measured from the vertically up direction. The azimuthal quantum number is associated with quantization of direction in this plane (p. 30).

CROSS-SECTION (of a rope) The two-dimensional area or shape which is exposed when the rope is cut in a plane perpendicular to its length (p. 21).

DISCONTINUITY (in a wave) An abrupt change in value at some point in space or time. The amplitude of the wave has a completely different value at two points very close to the discontinuity point, but on opposite sides of it, no matter how close the two points are to each other (p. 17).

DISCRETE Separate, not continuous, individually distinct (p. 12).

EXTRAPOLATE Extend previous data in order to guess the correct data in a range outside that previously known. In this Unit it is applied to the act of guessing the correct three-dimensional expression from a knowledge of the relevant expressions in one and two dimensions (p. 27).

FUNCTION (mathematical) A mathematical expression the value of which usually depends on the values of other quantities; it is often, but not always, a simple algebraic combination of them. In this Unit its value always varies smoothly with the quantities on which it depends. Note, however, that this is not a mathematically rigorous definition of a function (p. 15).

INTEGER A whole number whether negative, zero or positive. An integral multiple of a quantity is that quantity multiplied by a whole number (p. 15).

PLANE An imaginary flat surface extending indefinitely in all directions (p. 16).

PULSE A single disturbance of very short duration. In a rope pulse, the disturbance is a transverse movement of the rope. A pulse is a special kind of wave (p. 9).

TRAIN (of pulses) A continuous succession of pulses which form a wave. Although not explicitly stated you should imagine that each pulse has such a shape that when they are joined together they form the shape of a conventional wave—mathematically the shape of a sine graph (p. 10).

Section 30.2

You should not necessarily attempt all the questions, but select those that you think will help you the most. The association of a particular objective with a question should not be taken to imply that the question tests that objective completely.

Question 1 (*Objective 1*)

In a total of not more than about 100 words distinguish clearly between the following terms, using rope waves to illustrate their meanings: normal mode, overtone, harmonic, resonance.

Question 2 (*Objective 2*)

Someone asks you to explain why a stretched rope with both ends clamped will only vibrate easily at certain discrete frequencies and how these frequencies are related to each other. Select from the following list those statements which are both true and directly relevant to your explanation.

- (a) Waves of all frequencies travel along the rope with the same speed.
- (b) In a stationary wave on a rope there is no net flow of energy in either direction along the rope.
- (c) The points of maximum displacement in a stationary wave are called antinodes.
- (d) The distance between consecutive points of zero displacement (nodes) is half the wavelength.
- (e) The wavelength can be calculated from the frequency using $v = \lambda f$.
- (f) There must be an exact number of half-wavelengths in the length of the rope.
- (g) The ends of the rope are nodes.
- (h) The possible wavelengths form a series in which each is an integral multiple of the wavelength of the fundamental mode of vibration.

Question 3 (Objective 3)

The velocity of transverse waves along a certain wire under tension is 150 m s^{-1} ; the length of the wire is 0.6 m . Complete the table below column by column without quoting an expression for the frequency (equation 3), but rather by fitting an integral number of half-wavelengths into the wire, and then calculating the wavelength (by doubling the half-wavelength) and the frequency (using $v = \lambda f$). The harmonic numbers should be found by inspection of the frequencies.

	$\frac{1}{2} \lambda$ (in metres)	λ (in metres)	f (in hertz)	Harmonic
Fundamental				
1st Overtone				
2nd Overtone				
3rd Overtone				
4th Overtone				

Question 4 (Objective 4)

You wish to measure the velocity of sound in air at various temperatures and have narrowed your choice down to two methods:

- (a) A gun is fired to produce a sharp sound. Two microphones are placed, one near the gun, and the other about 30 m from the first one in a direction away from the gun. The first microphone triggers an oscilloscope and the second displays a pulse on the trace (as used in the muon decay experiment in Unit 2). The apparatus is used outside, and relies on changing weather conditions to get different temperatures.
- (b) A tube about 0.3 m long, closed at both ends, but with two small holes in the wall near the middle (Fig. 26), has a stationary sound wave set

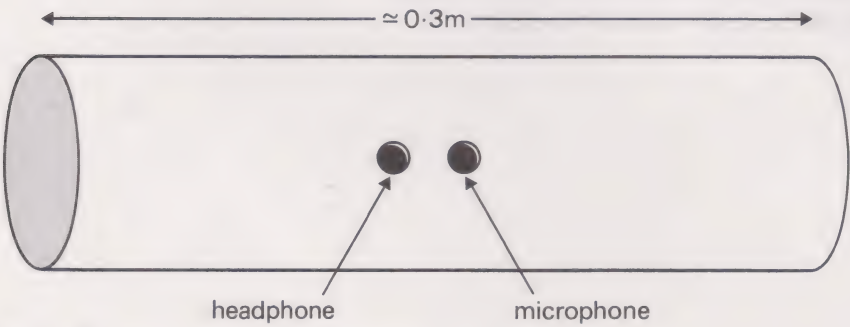


Figure 26 Resonance tube for measuring the velocity of sound.

up in it by placing a tiny headphone in one of the holes connected to a signal generator which produces a pure note of a single frequency. A microphone in the second hole is connected to a suitable instrument for measuring the intensity of the sound. As with a stretched rope, resonance occurs (giving a maximum sound output) when one half-

wavelength fits exactly in the tube. The frequency is measured to an accuracy of ± 1 Hz with a frequency counter and the velocity of the waves calculated from the product of wavelength and frequency. The temperature is pre-set to any desired value by placing the entire tube in a thermostated enclosure.

Think carefully about the two methods in relation to the probable accuracy of the result. Choose the one which you consider more suitable for a precise measurement of the velocity of sound. List its particular advantages (over the method you have rejected) for obtaining a precise and reliable value of the velocity of sound under known conditions. What measurement in the method you have chosen is likely to cause the greatest error in the result?

Question 5 (Objective 5)

The possible kinetic energies of an electron confined between a pair of parallel planes separated by a distance c are given by

$$T = n^2 \left(\frac{h^2}{8c^2 m_e} \right)$$

(The symbols have the same meanings as in equation 7 of the main text.)
What will be the effect on the zero-point kinetic energy if:

- (a) the separation of the planes is halved;
- (b) a proton of mass about 2 000 times that of an electron is confined between the planes instead of the electron?

Question 6 (Objective 5)

Classify the following statements according to the key below by selecting either (a), (b), (c), (d) or (e) for each.

- (a) Both assertion and reason are true statements and the reason is a correct explanation of the assertion.
- (b) Both assertion and reason are true statements but the reason is *not* a correct explanation of the assertion.
- (c) The assertion is true but the reason is a false statement.
- (d) The assertion is false but the reason is a true statement.
- (e) Both assertion and reason are false statements.

(i) ASSERTION

An electron confined in one dimension between one pair of parallel planes can only have discrete values of kinetic energy.

Reason

An exact number of electron wavelengths must fit between the two planes.

(ii) ASSERTION

The allowed kinetic energies of an electron confined between a pair of parallel planes are in the ratios 1:4:9:16, etc.

Reason

The allowed momenta of the electron are in the ratios 1:2:3:4, etc.

Question 7 (Objective 6)

An electron is confined between a pair of parallel planes; its potential energy varies with its position between the planes. It is in a high energy level, i.e. there are many possible lower energies. Select the correct alternative (a) or (b) in each of the following statements.

- (i) (a) Its kinetic energy is the same everywhere.
(b) Its total energy is the same everywhere.
- (ii) (a) The electron moves most slowly where its potential energy is greatest.
(b) The electron moves with the same speed everywhere.
- (iii) (a) The momentum of the electron is least where its potential energy is greatest.
(b) The momentum of the electron is greatest where its potential energy is greatest.
- (iv) (a) The wavelength of the electron is everywhere the same.
(b) The wavelength of the electron varies as its potential energy varies.
- (v) (a) The electron spends longer in regions of fixed length where it is moving slowly.
(b) The electron spends the same time in a region of fixed length whatever its speed.
- (vi) (a) The probability of finding the electron is greatest where its potential energy is greatest.
(b) The probability of finding the electron is greatest where its kinetic energy is greatest.
- (vii) (a) The wave-function of the electron has the same amplitude everywhere.
(b) The wave-function of the electron has a greater amplitude where its potential energy is greater.

Section 30.3

Question 8 (Objective 9)

Explain briefly why two quantum numbers are necessary to specify all the normal modes of a rectangular membrane.

Question 9 (Objective 10)

Classify each of the following statements as true or false.

- (i) The frequencies of normal modes on a stretched rope fixed at both ends are never degenerate.
- (ii) The definition of a degenerate frequency is one which corresponds to two or more different normal modes (with different quantum numbers).
- (iii) A square membrane has a higher proportion of degenerate frequencies than a rectangular one with unequal sides.

Section 30.4

Question 10 (Objective 10)

The wavelengths of jelly waves in a rectangular box are given by equation 13.

$$\frac{1}{\lambda^2} = \left(\frac{l}{2a}\right)^2 + \left(\frac{m}{2b}\right)^2 + \left(\frac{n}{2c}\right)^2$$

and from this the frequencies of the normal modes are easily found.

- If the box has equal sides (i.e. it is a cube) what are the quantum numbers of the normal modes having the lowest degenerate frequency; of what order is the degeneracy?
- Write down the quantum numbers of the lowest non-degenerate frequency of a cubical box.

Question 11 (Objective 7)

In the simple model of a hydrogen-like atom described in section 30.4.2, the kinetic energy T , the potential energy PE , and the mean radius r_1 are given by:

$$T = \frac{3h^2}{32m_e r_1^2} \dots\dots\dots(15)$$

$$PE = -\frac{Zq^2}{4\pi\epsilon_0 r_1} \dots\dots\dots(16)$$

$$r_1 \approx \frac{h^2 \epsilon_0}{m_e Z q^2} \dots\dots\dots(17)$$

What is the effect on the average value of each of these three quantities if an ion with $Z=4$ (but only one electron) is considered instead of hydrogen?

Section 30.5

Question 12 (Objective 8)

The way in which the electron wave function ψ varies with radius in the $n=3, l=1$ state of hydrogen is shown in Figure 27. You should remember that ψ depends on direction as well as radius in states for which l is not zero; this variation is not shown.

Use this to sketch the way in which the radial probability P_r of finding the electron in a shell of given thickness depends on the radius r of the shell.

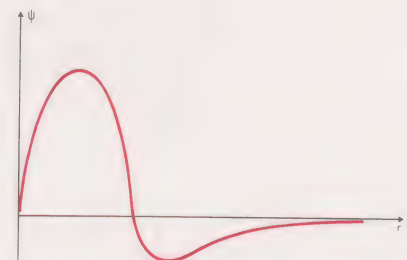


Figure 27 Radial part of the electron wave function of hydrogen in the $n=3, l=1$ state.

Question 13 (*Objectives 8, 10*)

Match each statement with the best reason:

- (1) The energy levels of an electron in a hydrogen atom are degenerate . . .
- (2) Energy is radiated by a hydrogen atom in discrete and definite amounts of various sizes . . .
- (3) The wavelength of the electron probability wave (wave function) in a hydrogen atom gets longer at larger radii . . .

BECAUSE . . .

- (a) of a 'mathematical accident' by which the potential energy of an electron varies in just the right way.
- (b) of the way in which the kinetic energy and momentum vary.
- (c) the energy levels have particular values characteristic of the atom.

A general question

Question 14 (*Objective 10*)

Explain in not more than two or three lines each what is meant by:

- (i) a degenerate frequency;
- (ii) a degenerate energy level.

Give one example of each.

Give another example of degeneracy in a completely different context.

Self-Assessment Answers and Comments

Question 1

A stretched rope clamped at both ends will only vibrate freely at certain frequencies; these frequencies and the associated rope patterns are called the *normal modes* of the rope. The lowest frequency is called the fundamental (mode) and others are called *overtones*. When the frequency of an overtone mode is an exact multiple of the fundamental, say 3 times it, that mode is also called the 3rd *harmonic*. The response of the rope in one of its normal modes when coupled to a source of vibration of the right frequency is called *resonance*.

Question 2

The true and directly relevant statements (in a logical order) are:

- (d) essential in conjunction with
- (g) to establish the truth of
- (f) which gives the discrete wavelengths which are possible.
- (a) is also necessary to establish how the frequencies are related given the wavelengths
- (e) allows frequencies to be calculated from wavelengths.

Other statements:

- (b) and (c) are true but not relevant.
- (h) is untrue.

The key quantitative statement in your argument will be (f), and from it you will derive the possible frequencies. (g) is necessary as a foundation for (f) because without it you cannot deduce that an integral number of half-wavelengths fits into the length of the rope. (d) is the other foundation for (f); without it, no quantitative statement about the wavelength can be made at all. The relation between the frequencies can be derived directly from (f) but it includes the velocity of waves along the rope; (a) is therefore necessary so that the frequencies may be related to each other quantitatively. However, (a) would not be necessary if you only wished to establish that the frequency is quantized.

- (b) Is irrelevant because the flow of energy is a more advanced problem than the motion of the wave itself; the concept of energy flow has nothing to do with the calculation of the normal mode frequencies of the rope.
- (c) Is a definition of a term—one which is not even necessary to the argument. Nodes on the other hand are an important part of your argument and a definition of 'node' might be judged relevant.
- (e) The equation $v = \lambda f$ is used to calculate the frequency, not the wavelength, in a derivation of the normal mode frequencies.
- (h) The wavelengths of normal modes with higher frequencies are smaller, not larger, than the wavelength of the fundamental mode. They cannot therefore be integral multiples of it; they are, in fact, integral submultiples— $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, etc.

Question 3

	$\frac{1}{2}\lambda$ (in metres)	λ (in metres)	f (in hertz)	Harmonic
Fundamental	0.6	1.2	125	(Fundamental)
1st Overtone	0.3	0.6	250	2nd
2nd Overtone	0.2	0.4	375	3rd
3rd Overtone	0.15	0.3	500	4th
4th Overtone	0.12	0.24	625	5th

Calculate the half-wavelength ($\frac{1}{2}\lambda$) by dividing the length 0.6 m by 1 (for the fundamental), 2 (for the first overtone), 3, 4 and 5 in order to fit an exact number of half-wavelengths into the rope. The wavelength λ is then twice $\frac{1}{2}\lambda$.

Calculate the frequency f from $f = \frac{v}{\lambda} = \frac{150}{\lambda}$. Thus, for example, if λ

is 0.3 m, $f = \frac{150 \text{ m s}^{-1}}{0.3 \text{ m}} = 500 \text{ s}^{-1}$ (or Hz).

The final column is obtained by writing the ratio of the frequency to the fundamental frequency—this is the definition of the harmonic. Thus

500 Hz is the $\frac{500}{125} = 4\text{th}$ harmonic, and so on.

Question 4

Both methods are perfectly feasible in principle. With a speed of sound of the order of 300 m s^{-1} , the time to be measured in method (a) is roughly 0.1 s ; the duration of the sound pulse itself is not likely to be much shorter than 10^{-3} s and the instant of triggering the oscilloscope will be uncertain to this extent. Timing errors will therefore be perhaps one per cent, subject to calibration of the oscilloscope time-base which will in practice rarely be this good. It should easily be possible to measure the resonance frequency in method (b) to one per cent accuracy. We favour method (b) for this reason and also for those given below.

Advantages of method (b)

- (1) Greater accuracy of measurement (see below under 'measurement causing the greatest error').
- (2) Much better control over temperature which can easily be kept even throughout the tube. This would be difficult over the extended path of method (a).
- (3) Much wider range of temperature possible, and without having to wait.
- (4) Control in principle over humidity which does affect the result slightly.
- (5) Repeatability of experiment. Laboratory conditions can be precisely reproduced, whereas conditions outside cannot.
- (6) Measurement is made at a single frequency. By using normal modes of higher frequency, it is possible to test for variation of the velocity of sound with frequency. The sharp pulse, in contrast, already contains a wide range of different frequencies, and high intensity also affects velocity.
- (7) Freedom from errors due to wind. In method (a) a light breeze could cause a one per cent increase in the velocity of sound measured 'down wind'.

Measurement causing the greatest error

Only two measurements are made in method (b):

the length of the tube (equal to one half-wavelength), and the frequency of resonance.

The length can certainly be measured to an accuracy of 0.1 per cent.

The frequency of the signal generator ($\approx 560 \text{ Hz}$) can be measured much more accurately than this if desired, but the sharpness of the resonance determines how accurately it can be *set*. The measurement causing the greatest error is therefore likely to be that of the true resonance frequency. We would, however, still expect to be able to determine this to a considerably greater accuracy than one per cent; hence this method is more accurate than method (a).

Question 5

The zero-point kinetic energy T_1 is equal to the value of T when n is one:

$$T_1 = \frac{h^2}{8c^2m_e}$$

- (a) The zero-point kinetic energy is four times as great.

[h (Planck's constant), m_e (the electron's mass) and the number 8 do not vary.]

$$\therefore T_1 \propto \frac{1}{c^2}$$

If the separation c of the two planes is halved, the zero-point kinetic energy T_1 is multiplied by $\frac{1}{(\frac{1}{2})^2} = 4$.]

- (b) The zero-point kinetic energy is smaller by a factor of about 2 000.

[h (Planck's constant), c (the separation of the two planes) and the number 8 do not vary.]

$$\therefore T_1 \propto \frac{1}{m_e}$$

If a proton of mass about 2 000 times that of an electron is used, the zero-point kinetic energy is multiplied by $\frac{1}{2\,000}$.]

Question 6

- (i): (c) The 'assertion' is true; the discrete values of kinetic energy are given by equation 7. The 'reason', however, is not a true statement. The electron wave is fitted between the two parallel planes in such a way that it has a node at each plane. Adjacent nodes are separated by one half-wavelength, so an exact number of electron half-wavelengths (not wavelengths, as in the question) must fit between the planes.
- (ii): (a) The 'assertion' is true; the values of the kinetic energy are given by equation 7 for $n=1, 2, 3, 4$, etc. Since $T \propto n^2$ (the other terms don't vary), the allowed kinetic energies are in the ratios 1:4:9:16, etc.

The 'reason' is also a true statement. The allowed values of momentum are given in Appendix 1 (Red):

$$p = \frac{nh}{2c}$$

Since h , c and 2 do not vary, p is proportional to n . So the allowed momenta are in the ratios 1:2:3:4.

The kinetic energies given by equation 7 are derived directly from the momentum, using equation 5:

$$T = \frac{p^2}{2m_e}$$

The 'reason' is, therefore, a correct explanation of the 'assertion'.

Question 7

Each pair of statements is mutually exclusive. In most cases this is obvious. If you are unsure about it in relation to the statements about energy, remember that in the absence of any external source of energy or a way of losing energy the total energy of any particle remains constant. Its total energy is made up of the sum of its kinetic and potential energies; it follows that any increase in, say, its potential energy is mirrored by a corresponding decrease in its kinetic energy.

- (i): (b) As stated above, it is the electron's total energy which is fixed. Its kinetic energy can vary provided that its potential energy also varies in such a way that their sum stays the same.
- (ii): (a) The electron's velocity v depends on its kinetic energy $\frac{1}{2}m_e v^2$. Since its potential energy varies, its kinetic energy is least where its potential energy is greatest (remember, their sum is fixed). The electron moves most slowly where its kinetic energy is least—i.e. where its potential energy is greatest.
- (iii): (a) The momentum $m_e v$ of any particle is least when its velocity v and kinetic energy $\frac{1}{2}m_e v^2$ are also least. From (ii) above, this is when its potential energy is greatest.
- (iv): (b) The wavelength λ of the electron is calculated from its momentum by the de Broglie formula

$$p = \frac{h}{\lambda}$$

Since its momentum varies as shown above in (iii) its wavelength must also vary. We leave you to work out where the wavelength is longest.

- (v): (a) The electron takes longer to traverse a region of fixed length if it is moving more slowly.
- (vi): (a) The probability of finding the electron in a spot-check of a particular region is obviously greater if the electron spends longer there. It spends longer in a region where it is moving more slowly—see (v) above—and it moves more slowly where its potential energy is greater—see (ii) above. So it is most likely to be found where its potential energy is greatest.
- (vii): (b) The amplitude of the wave-function ψ is determined by the fact that ψ^2 measures the probability of finding the electron in a region. This is greatest where its potential energy is greatest—see (vi) above. So the amplitude of the wave-function is greatest where the electron's potential energy is greatest.

Question 8

The wave can be separated into two parts, one representing a wave in each direction (parallel to a side) on the membrane. Each part must satisfy a boundary condition that an exact number of its half-wavelengths fits into the appropriate length; each condition leads to a separate quantum number.

You may want to take this question a bit further and ask yourself why one quantum number is not enough and three are unnecessary. The two parts of the membrane wave may be considered quite separately and represent two unrelated aspects of the wave which may be specified independently. Equation 11 for the normal mode frequencies of the membrane, therefore, contains two arbitrary constants (the quantum numbers m and n). If only one quantum number n is used, then m must be specified either by fixing its value, say at 2, or by relating it to n (perhaps equal to it). In either case, only part of Table 1 on p.22 is produced. In order to specify all the normal modes, two quantum numbers are necessary. A third quantum number, on the other hand, would be irrelevant. The normal modes are already completely specified by two quantum numbers.

Question 9

- (i) True. The wavelengths of the normal modes on a stretched rope are all different because each normal mode has a different number of half-wavelengths which fit exactly into the length of the rope. The frequency is obtained from the wavelength by using $v = \lambda f$. Since the velocity v of waves of all frequencies is the same, it is not possible to have two or more normal modes (having different wavelengths) with the same frequency. Degenerate frequencies are not, therefore, possible.
- (ii) True. A degenerate frequency is one which corresponds to *any* number of normal modes. There are different combinations of quantum number which correspond to the same frequency.
- (iii) True. A square membrane is symmetric in the sense that it can be rotated through ninety degrees and look the same. Thus the normal mode with, say, $m=3, n=1$ is indistinguishable from the normal mode with $m=1, n=3$ if the membrane is rotated. Clearly the frequencies must be the same and so correspond to one degenerate frequency. More quantitatively, from equation 11, for a square membrane the frequency f can be written

$$f \propto (m^2 + n^2)$$

The two quantum numbers m and n can be interchanged without changing f . Hence any frequency corresponding to a normal mode with unequal quantum numbers is a degenerate frequency, as in the example above. Frequencies corresponding to $m=n$ may or may not be degenerate. For example, the normal mode with $m=n=1$ is not degenerate but that with $m=n=5$ is (try $m=1$ and $n=7$). Table 1 on p.22 shows that most of the frequencies of a membrane with unequal sides are not degenerate; in fact the example in Table 1 has more degenerate frequencies than other examples because of the simple ratio between the lengths of its sides. Clearly, therefore, a square membrane has a higher proportion of degenerate frequencies than a membrane with unequal sides.

Question 10

- (i) For jelly waves in a cubical box (section 30.4.1) the normal mode with the lowest quantum numbers ($l=m=n=1$) is not degenerate. The next lowest frequency corresponds to three normal modes having the following quantum numbers:

l	m	n
2	1	1
1	2	1
1	1	2

The order of the degeneracy is 3 because there are 3 normal modes with the same lowest frequency.

- (ii) The only non-degenerate frequencies have all three quantum numbers equal. The lowest non-degenerate frequency corresponds to the longest wavelength and smallest quantum numbers:

$$l=m=n=1$$

Question 11

Notice that the kinetic energy and potential energy both depend on the value of the radius, now set at r_1 . If you did not see this you will have got the wrong answers for these two quantities.

Take the radius first. All the terms except Z in equation 17 are fixed in value, so

$$r_1 \propto \frac{1}{Z}.$$

If Z is increased from 1 to 4, the radius r_1 is reduced by a factor 4.

Now the kinetic energy. Leaving out the terms which are fixed, equation 15 becomes

$$T \propto \frac{1}{r_1^2}.$$

If r_1 is reduced by a factor 4, T must be increased by a factor 16.

Finally, the potential energy. Equation 16 reduces to

$$PE \propto \frac{Z}{r_1}$$

Z is increased from 1 to 4 and r_1 is reduced by a factor 4, so the potential energy is increased by a factor 16.

Question 12

The relationship between P_v and P_r is expressed graphically by the examples in Figure 19. More quantitatively

$$P_v = \psi^2$$

and

$$P_r = 4\pi r^2 \psi^2.$$

Although you are only asked to sketch P_r , you will probably have chosen to draw P_v first though it is not actually necessary. We show all three graphs in Figure 28.

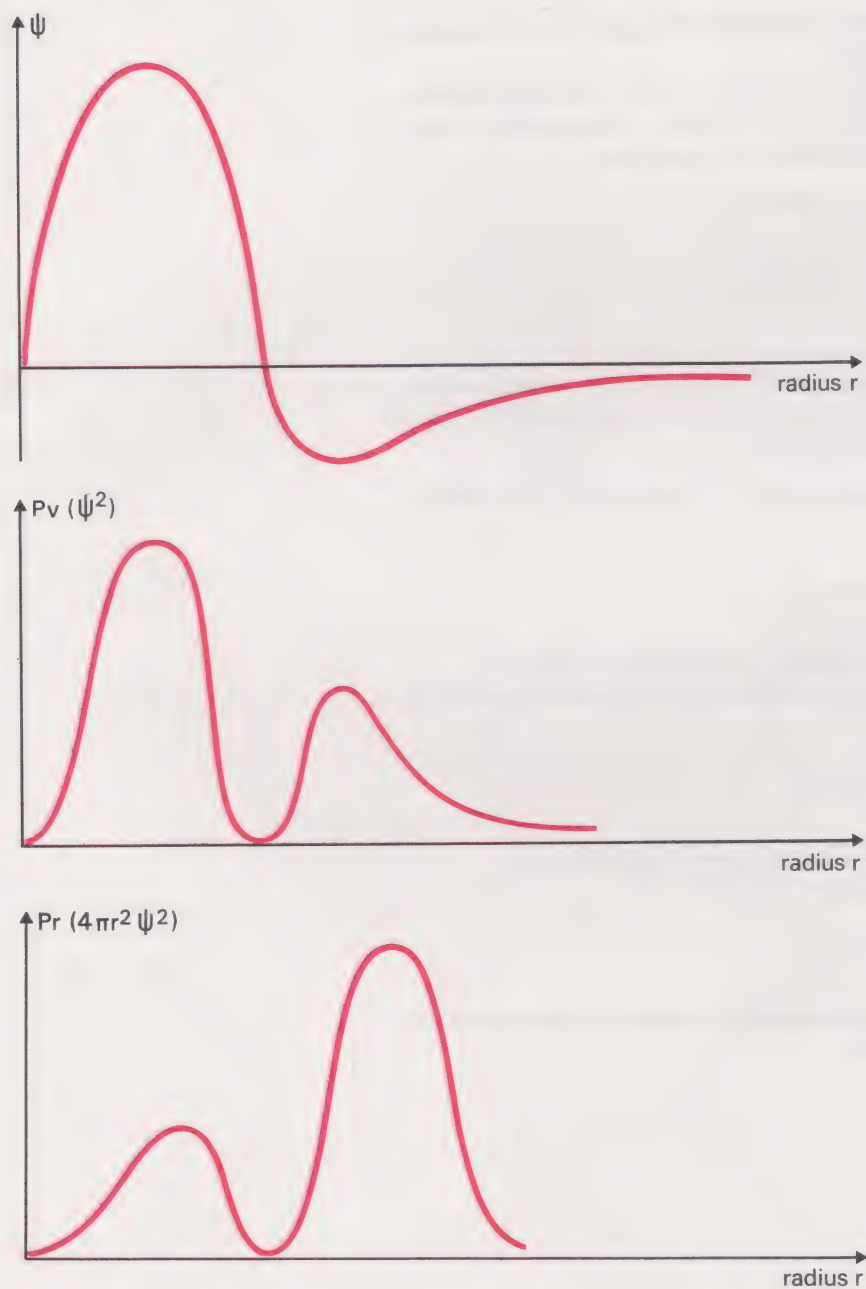


Figure 28 Electron wave function and probabilities for the $n=3, l=1$ state of hydrogen.

Notice especially the shape of the graphs of P_r and P_v near the horizontal axis, and the reversal of the heights of the two peaks in the P_r graph due to the factor r^2 which has a greater effect at larger radii. Both these features are also apparent in Figure 19.

Question 13

(1) and (a), (2) and (c), (3) and (b).

Some of the statements make reasonable sense when paired differently, but not all of them simultaneously.

Take statement (2). A reason is needed for the existence of 'discrete and definite amounts' of radiated energy. (a) and (b) do not provide such a reason; (c) does. So (c) must be right for this one.

Now take statement (3). The reason for the increase of wavelength with radius is obtained from the de Broglie formula $p = \frac{h}{\lambda}$; it is that the momentum gets smaller. This in turn depends on the kinetic energy being smaller and the potential energy larger. (a) makes some sense, but implies more than is necessary—the potential energy only needs to increase, not to vary in a particular way. (b) makes better sense. (c) would make no real sense at all because the wavelength is not determined by the total energy.

Statement (1) is a very precise statement about the equality of energy of states having the same value of n but different values of l (and m). It requires a precise reason and only (a) provides one. This also excludes (a) from statement (3), leaving (b) as correct for that statement.

Question 14

- (i) A degenerate frequency (in a system which can vibrate) is a frequency associated with more than one normal mode.

E.g. Jelly waves in a cubical box (equal sides):

$$\left. \begin{array}{l} l=1, m=2, n=3 \\ l=1, m=3, n=2 \\ l=2, m=1, n=3 \\ \text{etc.} \end{array} \right\} \text{all have the same frequency.}$$

- (ii) A degenerate energy level is an energy level associated with more than one state (set of quantum numbers).

E.g. The hydrogen atom. In the absence of a magnetic field (see p. 00), all states with the same values of l and m have the same energy, making that energy level degenerate.

$$\left. \begin{array}{l} n=2, l=1, m=0 \\ n=2, l=1, m=-1 \\ n=2, l=1, m=1 \\ n=2, l=0, m=0 \end{array} \right\} \text{all have the same energy.}$$

A different example:

In the genetic code, the amino acid glycine is represented by

GGU

GGC

GGA

and GGG

with the usual notation for the bases. The genetic code is degenerate.

There are, of course, many other possible examples in both parts of the question.

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